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Bench-Scale Studies to Identify Process Parameters Controlling Reburning with Pulverized Coal

Energy and Environmental Research Corp., Irvine, CA

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BENCH-SCALE STUDIES TO IDENTIFY PROCESS PARAMETERS CONTROLLING REBURNING WITH PULVERIZED COAL

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16. ABSTRACT

The report addresses the evaluation of a technology which is a combination of two technologies used to control the atmospheric emission of NOx by stationary sources: (1) combustion modification (controls flame temperature and maximizes fuel-rich residence time to minimize NOx formation); and (2) flue gas cleaning (uses a reducing agent with or without a catalyst to remove NOx from combustion products). The combined technology uses fuel as a reducing agent to remove NOx. The process (referred to as in-furnace NOx reduction, reburning, and staged fuel injection) can be applied to many types of combustion systems. In fact, reburning is the process which allows the "in-furnace NOx reduction" to take place. Reburning involves two processes: (1) NO reduction (reburning fuel is added to the combustion products of the main combustion zone, which operates fuel lean, to produce a fuel-rich mixture, products of which are referred to as total fixed nitrogen); and (2) TFN oxidation (air is added to produce overall fuel-lean conditions, with the NH3, HCN, NO, and char nitrogen converted to either N2 or NO and fuel oxidation completed).

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Nitrogen Oxides		Stationary Sources	07B
Coal	Pulverized Fuels	Reburning	21D
Combustion		Staged Fuel Injection	21B
Reduction (Chemistry)			07C
Oxidation			

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1.0 EXECUTIVE SUMMARY

This report summarizes the results of a small theoretical and experimental study which was undertaken as part of the EPA's Fundamental Combustion Research Program to investigate in-furnace NO_x reduction (reburning). In simple terms, the reburning concept involves the use of a heat release zone (via staged furl addition) to convert NO formed earlier in the main combustion zone into some form which will ultimately produce N_2. The process takes place in two discrete zones.

1. NO Reduction Zone. Here fuel is added to produce CH radicals which reduce part of the NO from the main combustion zone to N_2, HCN, and NH_3.
2. XN Oxidation Zone. Here the final combustion air is added and a percentage of the total fixed nitrogen (TFN) pool (HCN + NO + NH_3) and char nitrogen (if any) are oxidized to NO as the remaining fuel fragments burn to CO_2 and H_2O.

Thus, NO can produce N_2 in both zones and the key to reburning is to provide the species and temperatures which allow this to happen. The first zone forms N_2 but also converts NO into species which can also be converted to N_2 in the second zone.

Figure 1-1 shows data obtained by Takahashi (1981) and coworkers with coal firing and it demonstrates the overall potential of the reburning concept (referred to as Mitsubishi Advanced Combustion Technology, or MACT, by the Japanese researchers). This figure also shows data obtained in the boiler simulator furnace (BSF) at Energy and Environmental Research Corporation (EER). Both sets of data indicate that it is possible to achieve extremely low levels (50 ppm NO_x at 6 percent O_2) under ideal combustion conditions; and, in general, it has been possible to reproduce the Japanese results under similar test conditions in the United States. However, the application of reburning to large-scale commercial systems in the U.S. burning a wide range of bituminous and low-rank coals is not as simple as Figure 1-1 suggests. In the reburning process NO can produce N_2 in both zones and to optimize the process it is necessary to provide the species and temperatures which maximize the rate of N_2 formation. Some NO is reduced to N_2 in the first zone, but the remaining NO either remains as NO or is converted into species which are capable of being reoxidized in the second stage.

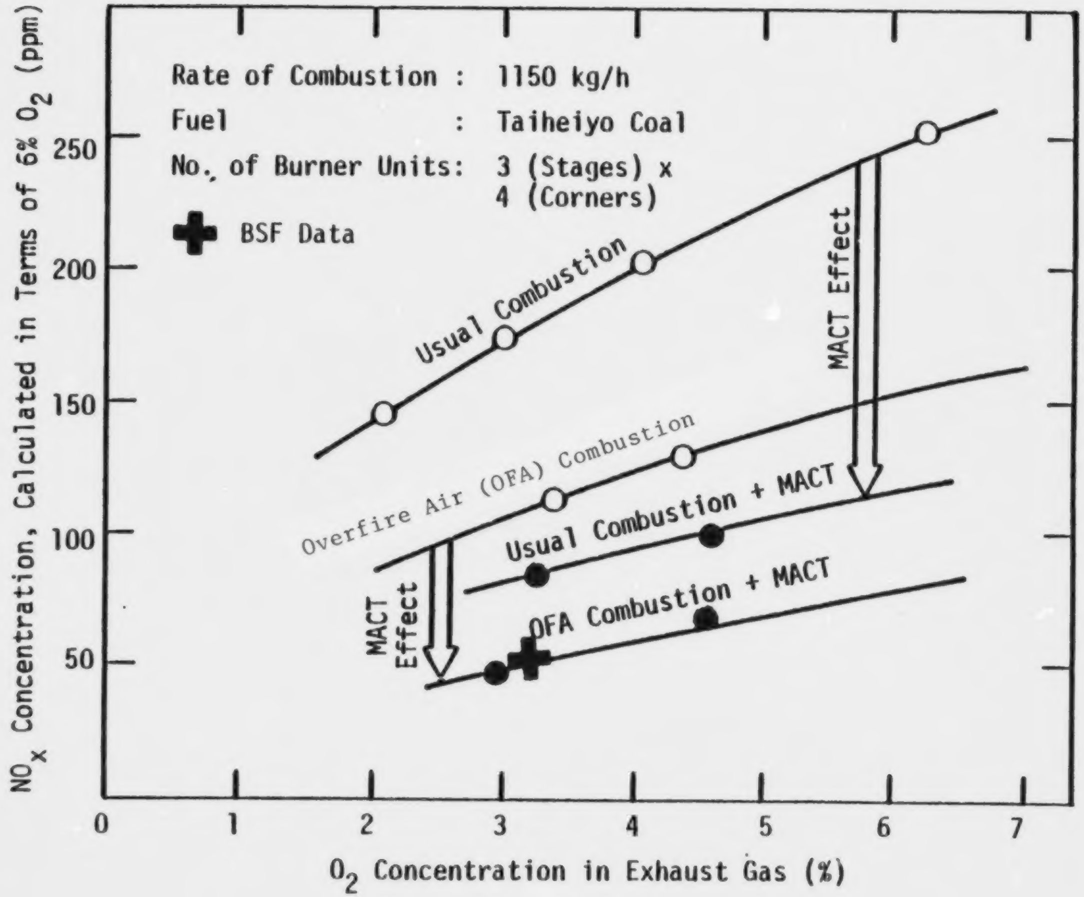


Figure 1-1. NO_x Removal Effect for Coal Firing.

To investigate the optimization and application of the reburning process, experimental studies were conducted in two facilities: a 2.25-inch ID, 7000 Btu/hr, back-fired, laboratory reactor firing doped gaseous fuels and a 6-inch ID, 70000 Btu/hr, tunnel furnace firing pulverized coal. The reburning fuels used in this investigation included propane, North Dakota lignite, bituminous coals from Utah and Alabama, and Australian version coal.

The principal conclusion of the work can be summarized as follows:

NO Reduction Zone

1. The optimum rich zone stoichiometry (SR_2) is approximately 0.9 because of the tradeoff between NO reduction and increased concentration of easily oxidizable N species. Figure 1-2 compares the data from several sources and attests to the consistency of the overall conclusion. At stoichiometries leaner than 0.9, the initial NO is not reduced as effectively perhaps because of a lack of CH radicals. At rich-zone stoichiometries below approximately 0.9, large amounts of TFN species (particularly HCN and NH_3) are produced and ultimately oxidized to NO in the final stage. As Figure 1-2 indicates, this problem is greatly enhanced in the case of coal where the reburning fuel nitrogen becomes more significant as additional reburning fuel is added.
2. The primary zone stoichiometry (SR_1) has little influence on the exhaust NO at the optimum reburning conditions. Increasing SR_1 only slightly decreases the effectiveness of the reburning concept in spite of a large increase in the available reactive nitrogen in the rich zone (due to increased reburning fuel).
3. The nitrogen content of the reburning fuel has only a small effect on the reburning efficiency at optimum combustion conditions, but at lower rich zone stoichiometric ratios, it can be of major importance. Figure 1-3 shows data obtained with doped propane flames and indicates that at rich zone stoichiometries below approximately 0.8, the nitrogen content of the reburning fuel greatly influenced the effectiveness of the reburning concept. This is of particular importance because a large-scale utility system would inevitably have a distribution of rich zone stoichiometries across the combustion chamber in the reburning zone.

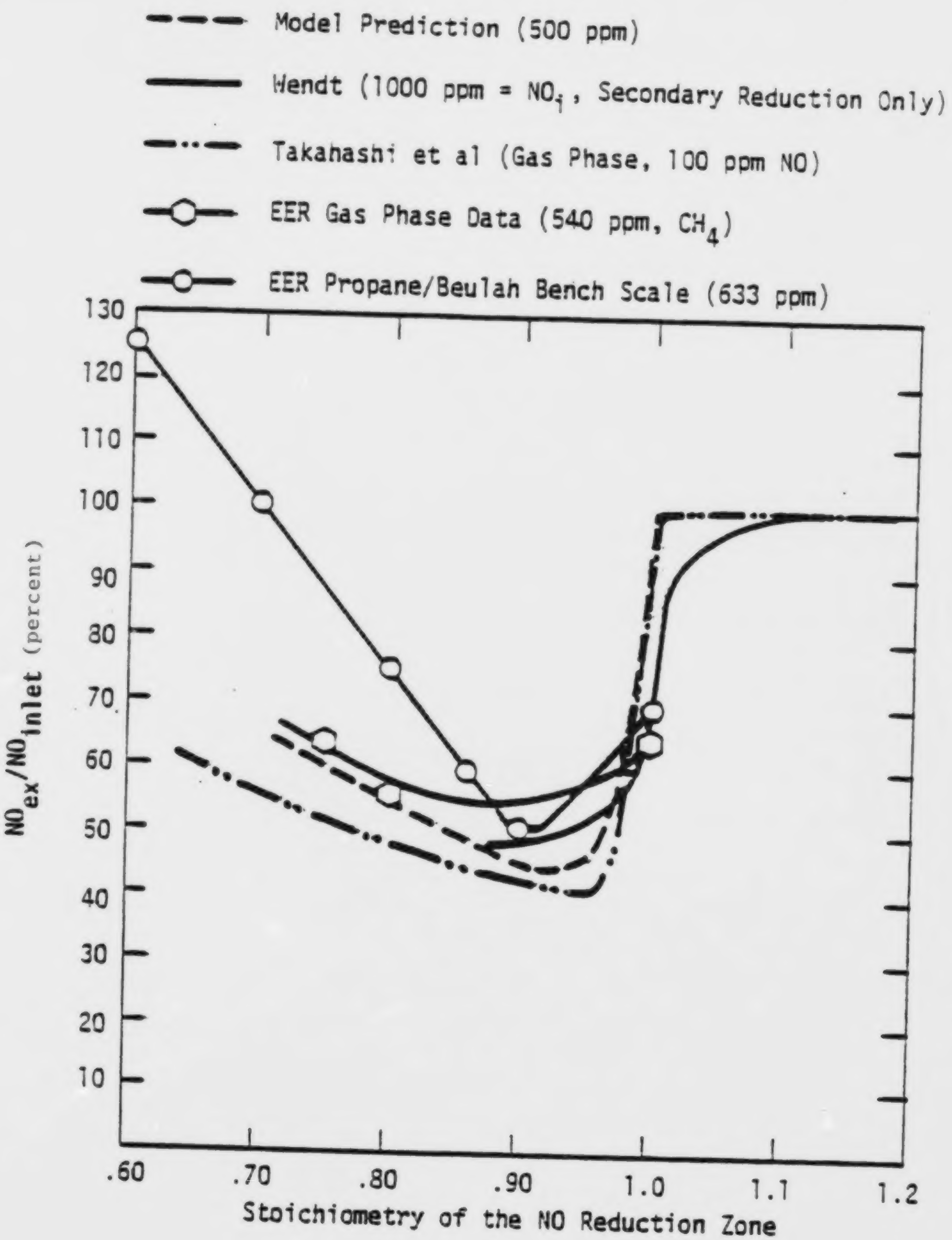


Figure 1-2. Effectiveness of Reburning - Subscale Data.

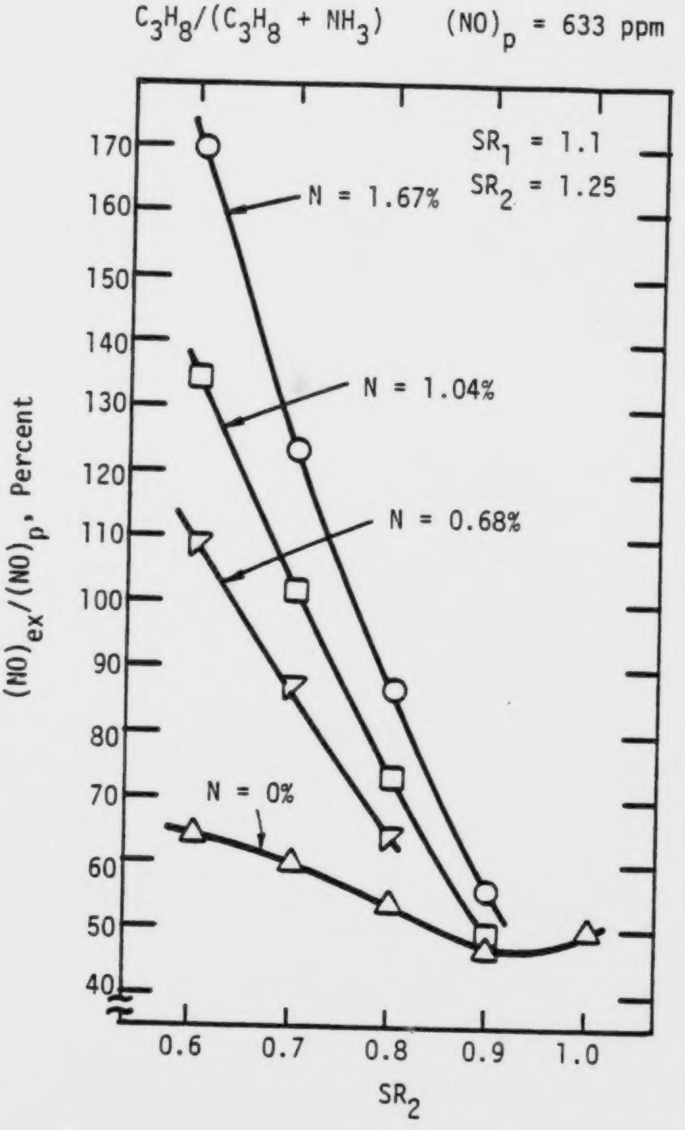


Figure 1-3. Effect of SR_2 and Reburning - Fuel Nitrogen Content (Tunnel Furnace).

4. The effectiveness of reburning depends strongly on the relationship of the initial NO concentration to the amount of reburning fuel nitrogen added to achieve an overall rich zone stoichiometry of 0.9. Figure 1-4 shows that even with optimum combustion conditions at low initial NO levels, reburning may actually increase exhaust NO emissions. With an initial NO level of approximately 150 ppm and a typical coal as the reburning fuel, the reactive nitrogen available in the rich zone increases almost fivefold when the reburning fuel is added to achieve an overall stoichiometry of 0.9.
5. The coal composition is important because it influences the char burnout, the initial NO level, and the reburning fuel nitrogen content and speciation. Many of the coals commonly being used in the United States for power generation may prove to be relatively unsuitable for reburning, particularly in retrofit applications, because it will not be possible to effectively burn out the coal char in the available time.

XN Oxidation Zone

1. The TXN (total fixed nitrogen, including char N) conversion depends on the XN speciation, the XN concentration, the hydrocarbon content at the rich zone exhaust, and the thermal environment.
2. Low XN conversions can be achieved by tailoring the temperature profile to obtain selective reduction of NO by NH_i species in the final, oxygen rich stage. Figure 1-5 summarizes the results obtained in the tunnel furnace and shows the dramatic influence of thermal environment on the effectiveness of the reburning concept for two initial NO levels. This effect is believed to be directly related to a large decrease in the TFN conversion in the final stage of the reburning process.

In summary, the overall processes controlling the reburning phenomena have been relatively well-identified and characterized. Although the elementary reactions are not fully understood at the present time, the key parameters have been identified and the overall mechanisms defined. Further work is needed to define the influence of mixing rates and establish the potential impacts of applying reburning to boilers and furnaces.

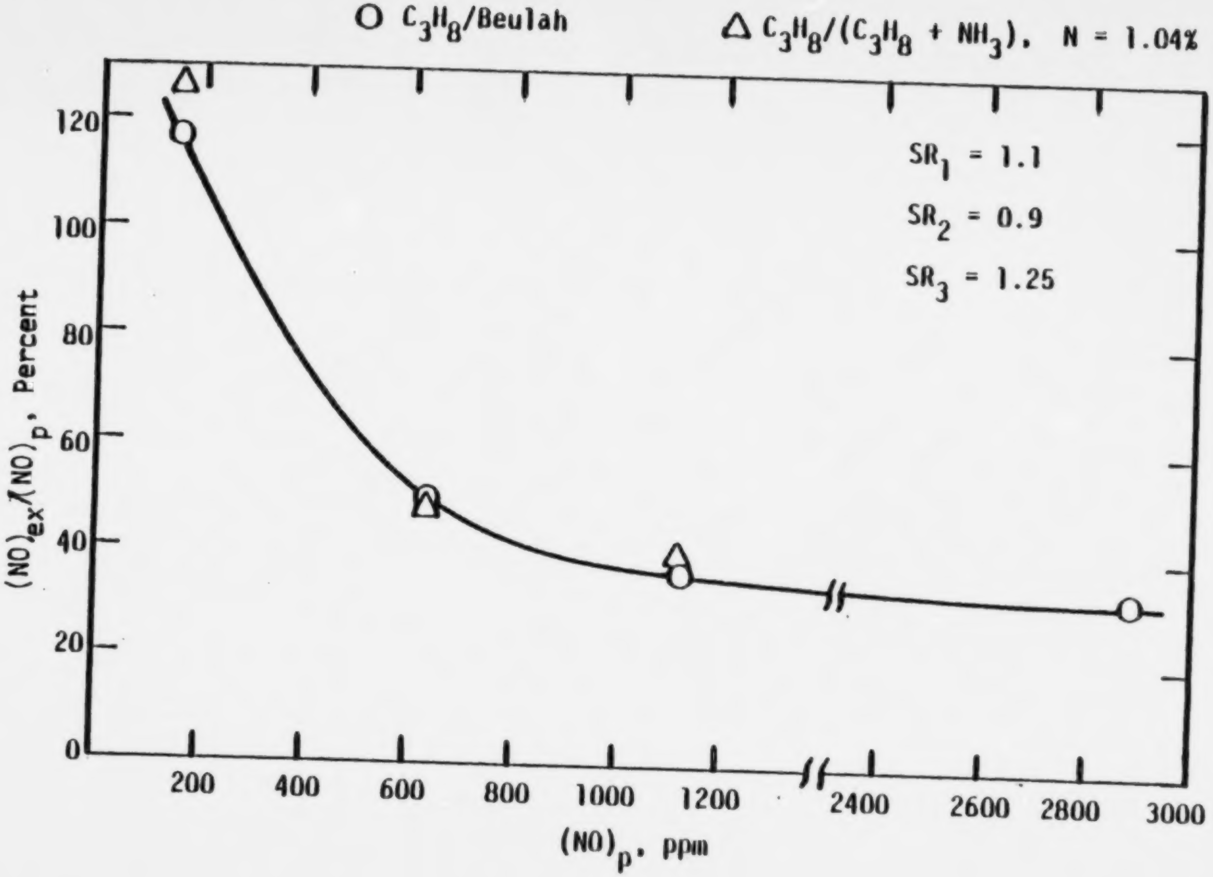


Figure 1-4. Influence of Reburning Fuel Type and Primary NO Level.

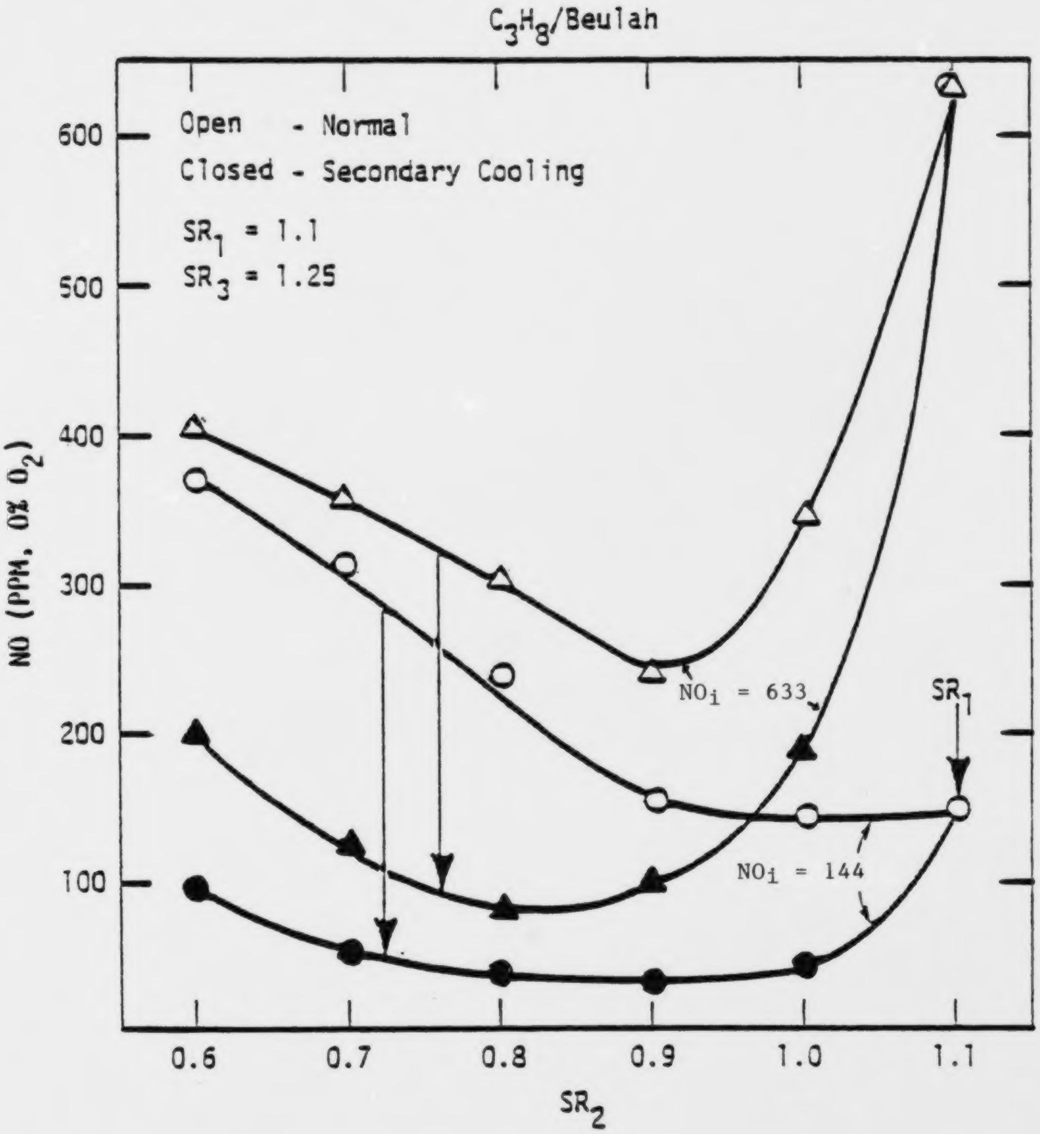


Figure 1-5. Effect of Secondary Cooling on Exhaust NO Emissions.

2.0 PROCESS DESCRIPTION

2.1 Introduction

Since it was first recognized that nitrogen oxides (NO_x) emitted by stationary sources made a significant contribution to the degradation of air quality, there have been considerable advances in the field of emission control technology to reduce emissions. The technology can be divided into two general classes:

- Combustion Modification. NO_x is formed as a consequence of the combustion process. Modification of that process to control flame temperature and maximize fuel rich residence times minimizes the formation of NO_x.
- Flue Gas Cleaning. This option involves the use of a reducing agent with or without a catalyst to remove NO_x from the combustion products.

This report addresses the evaluation of a technology which is a combination of the above. Fuel is used as a reducing agent to remove NO_x. The process is referred to as

- in-furnace NO_x reduction,
- reburning, and
- staged fuel injection;

and it can be applied to many types of combustion systems. In fact, reburning is the process which allows "in-furnace NO_x reduction" to take place.

The basic concepts associated with in-furnace NO_x reduction by reburning are not new. The reduction of NO by flames has been appreciated for over a decade. A flue gas NO_x incinerator was developed by the John Zinc Company (Reed, 1969). The term 'reburning' was coined by Wendt, Sternling, and Matovich (1973) who reduced NO produced in a laboratory scale flat flame by adding methane or ammonia to the combustion products. Recently, Japanese investigators have reported the application of reburning to large test furnaces and there are field demonstrations of the technology currently in progress (Takahashi, et al, 1981). The MACT (Mitsubishi Advanced Combustion Technology) in-furnace NO_x removal process applies the concept of reburning to a boiler. Part of the fuel bypasses the main heat release zone and is injected above the main burners to provide the fuel for reburning. It is claimed that the NO_x produced by the main firing system can be reduced "to half at any level of concentration. In an in-furnace NO_x reduction test using a low NO_x gas burner, NO_x emissions as low as 8 ppm (calculated at 5 percent oxygen) have been reported. Figure 2-1 illustrates the application of MACT to a corner-fired test furnace firing coal under normal main zone combustion conditions and in conjunction with overfire air NO_x control. Takahashi reports that irrespective of the fuel used for reburning, the NO_x level produced by the main combustion system is reduced by never less than 50 percent.

Reburning involves two separate processes:

- NO Reduction. The reburning fuel is added to the combustion products of the main combustion zone, which operates fuel lean, to produce a fuel-rich mixture. NO is reduced by hydrocarbon radicals to nitrogenous intermediates such as NH_3, HCN, etc. When the reburning fuel contains nitrogen (e.g., if the reburning fuel is coal) the coal nitrogen could remain with the char or form NO, HCN, and NH_3. Thus, the products of this first process contain nitrogen species which can be converted to NO; namely, char nitrogen, NH_3, and HCN, as well as NO. These gas-phase species will be referred to as total fixed nitrogen (TFN).
- TFN Oxidation. In the second step of the process, air is added to produce overall fuel-lean conditions. The NH_3, HCN, NO, and char nitrogen are either converted to N_2 or NO. In addition, since the first process requires overall fuel-rich conditions, fuel oxidation is completed in the second step.

Explained in this way, reburning appears to have many of the same features as staged combustion--a fuel-rich zone followed by a burnout zone. The attraction of reburning is associated with the claim that NO_x produced in the main combustion zone can be reduced by 50 percent. Thus, two possible control options exist:

- The main combustion zone could be fired with conventional burners, and the application of the reburning process should produce exhaust NO_x levels on the order of 225 ppm.

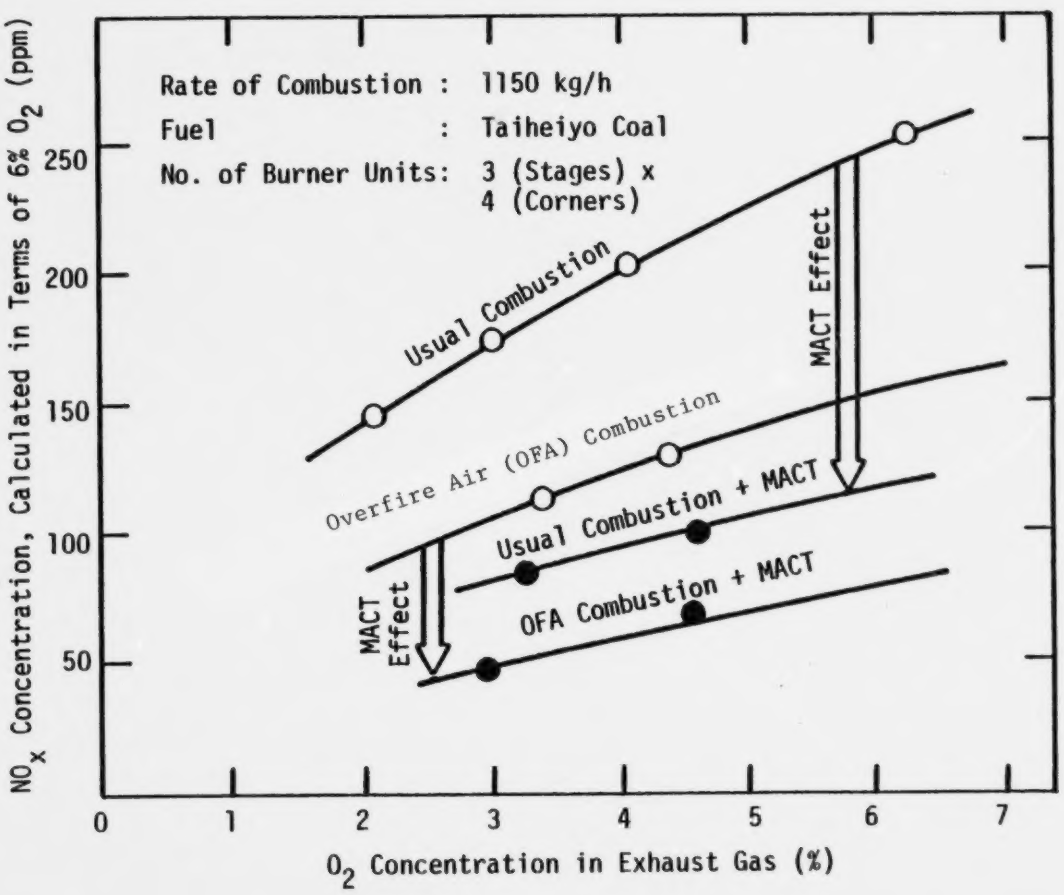


Figure 2-1. NO_x Removal Effect for Coal Firing.

- Low-NO_x burners could be used in the main combustion zone and exhaust NO_x levels of 100 ppm and below should be achievable with the application of reburning.

In the first option, depending on cost, reburning is an alternative to replacing conventional burners with low NO_x burners for the main firing system.

2.2 The Chemistry and Kinetics of Reburning

The gas-phase reactions associated with the reburning processes are well established. This fact is due to the extensive study of the gas-phase kinetics associated with similar processes such as staged combustion and thermal $DeNO_x$. The two separate processes of the reburning technique are illustrated in Figure 2-2: NO reduction in which primary NO partially reacts to form N_2 and intermediate species under rich conditions and XN conversion where TFN and the intermediate species are oxidized. Staged combustion similarly consists of two stages: a first stage which is operated rich in order to maximize conversion of fuel nitrogen to N_2 and a burnout stage where combustion is completed. Thermal $DeNO_x$ involves injection of ammonia at lower temperatures to effect a reduction of NO. Because no new species are being generated, and because the conditions are very similar, the reactions and kinetics developed for staged combustion and thermal $DeNO_x$ are directly applicable to reburning. This section will discuss that which can be implied from a consideration of equilibrium and kinetics of gas-phase reactions about the limits of reburning and the influence of controllable parameters.

It is generally true that under rich conditions, equilibrium levels of fuel nitrogen species are low. This fact implies that, given sufficient time under rich conditions, almost all nitrogen will convert to molecular nitrogen. Figure 2-3 is a plot of equilibrium levels of total fixed nitrogen species (HCN, NH_3, and NO) as a function of stoichiometry and temperature. Except for high temperatures (greater than 2000 K) and extremely rich conditions (SR <.5), the equilibrium levels are less than 10 ppm. However, under lean conditions, equilibrium levels can be significant, even for moderate temperatures (optimum 1800 K) under rich conditions or low temperatures near stoichiometric conditions.

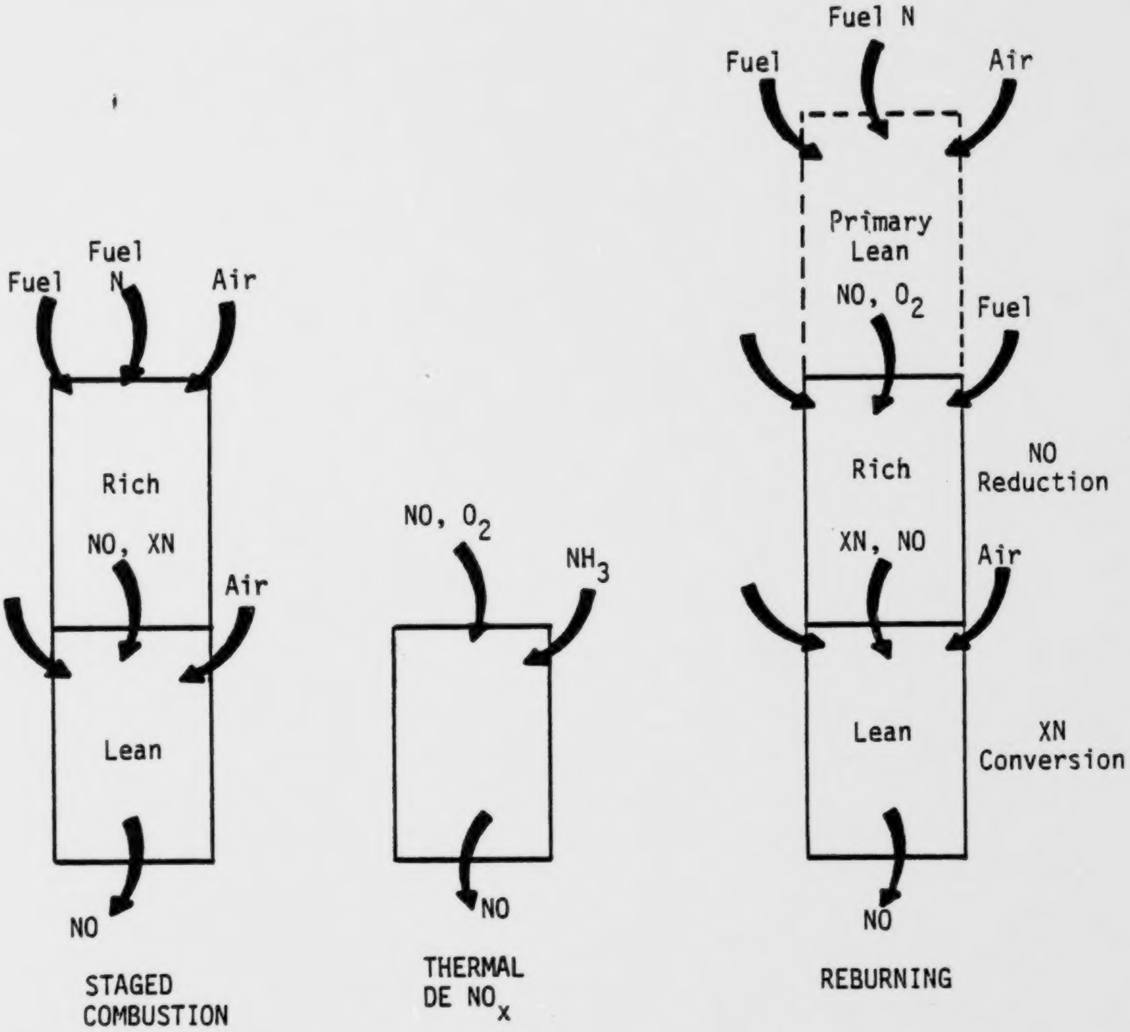

Fuel
Fuel N
Air
Rich
NO, XN
Air
Lean
NO
STAGED COMBUSTION
NO, O_2
NH_3
NO
THERMAL DE NO_x
Fuel N
Fuel
Air
Primary Lean
NO, O_2
Fuel
Rich
NO Reduction
XN, NO
Air
Lean
XN Conversion
NO
REBURNING

Figure 2-2. Low-NO_x Processes.

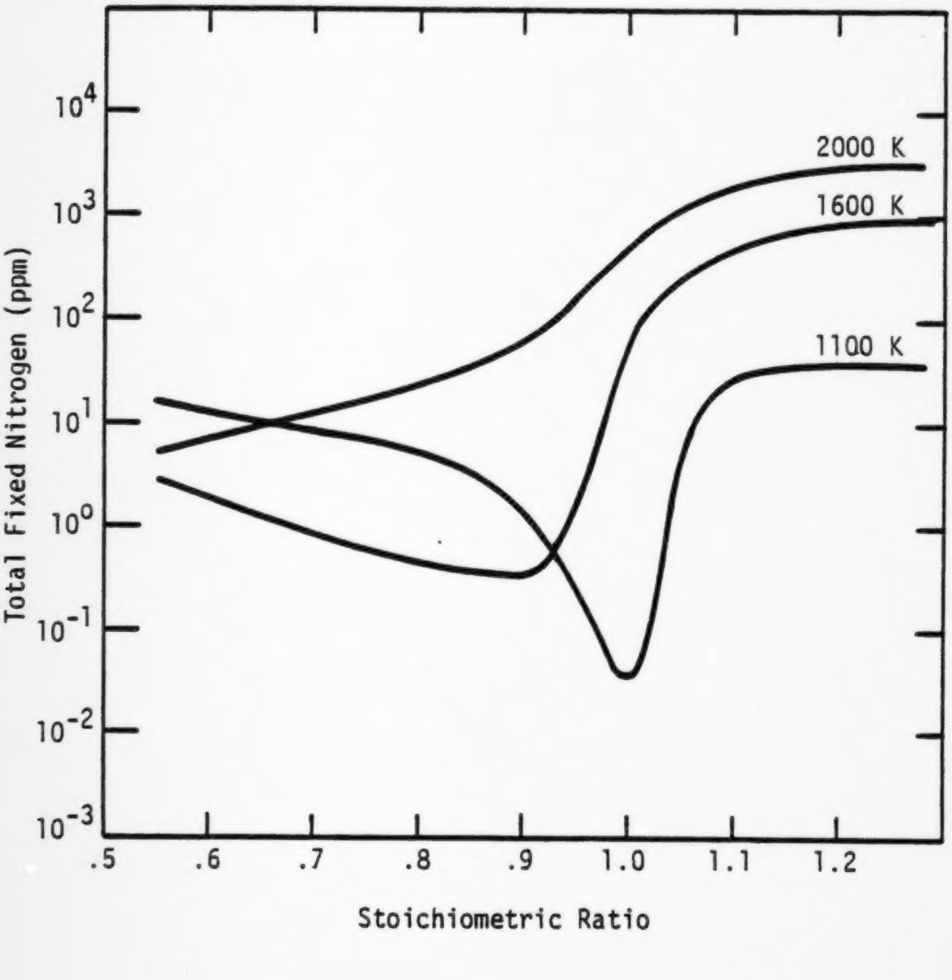


Figure 2-3. Equilibrium Fixed Nitrogen Species Concentrations.

In reality, the kinetics which dictate the speed at which the concentration levels approach equilibrium are slow. Therefore, despite the fact that equilibrium levels are low, the actual emission levels are much higher due to finite reaction rates and times. There are two ways that the reaction rates can be increased: increasing temperature and increasing the levels of reactive free radicals. Traditional staged combustion takes advantage of both of these by burning the fuel nitrogen species at high temperatures in a rich flame where free radical concentrations are high.

Reburning takes advantage of the latter approach by increasing the level of free radicals without significant modification to the temperature. Figure 2-4 is a schematic of the overall gas-phase reactions occurring in the reburning reduction zone. The hydrocarbon fuel reacts with oxygen to form hydrocarbon fragments such as CH, CH_2, and CH_3 which subsequently react with NO to form cyanide species. These cyanide species are coupled with the amine subset principally through NH. The amine species can then react in several ways depending on conditions. NH will react with OH, H, and O_2 to form either HNO or N at about equal rates. HNO breaks down relatively fast into NO; however, atomic nitrogen can either form NO (predominantly) or N_2. A secondary reduction path through NH involves the formation of the intermediate N_2O which is relatively unstable at high temperatures and rapidly decomposes to N_2.

This reaction scheme relies heavily on the contribution of free radicals. In particular, hydrocarbon reactions with oxygen form the methyl type radicals which initiate the entire process. The propagation of the chain of reactions relies primarily on H, OH, and O radicals which are also produced in the hydrocarbon combustion process. Thus, the approach towards the low equilibrium levels is accelerated by the higher free radical concentration generated by the secondary fuel oxidation.

The parameters expected to be of importance for effective reduction of NO in the secondary fuel injection stage are temperature, residence time, stoichiometry, and primary NO level. Because of the Arrhenius nature of the reaction rates, the rates increase exponentially with temperature. Since it is desirable to increase the rates as fast as possible in order to approach equilibrium levels, it is desirable to operate as hot as possible. However, equil-

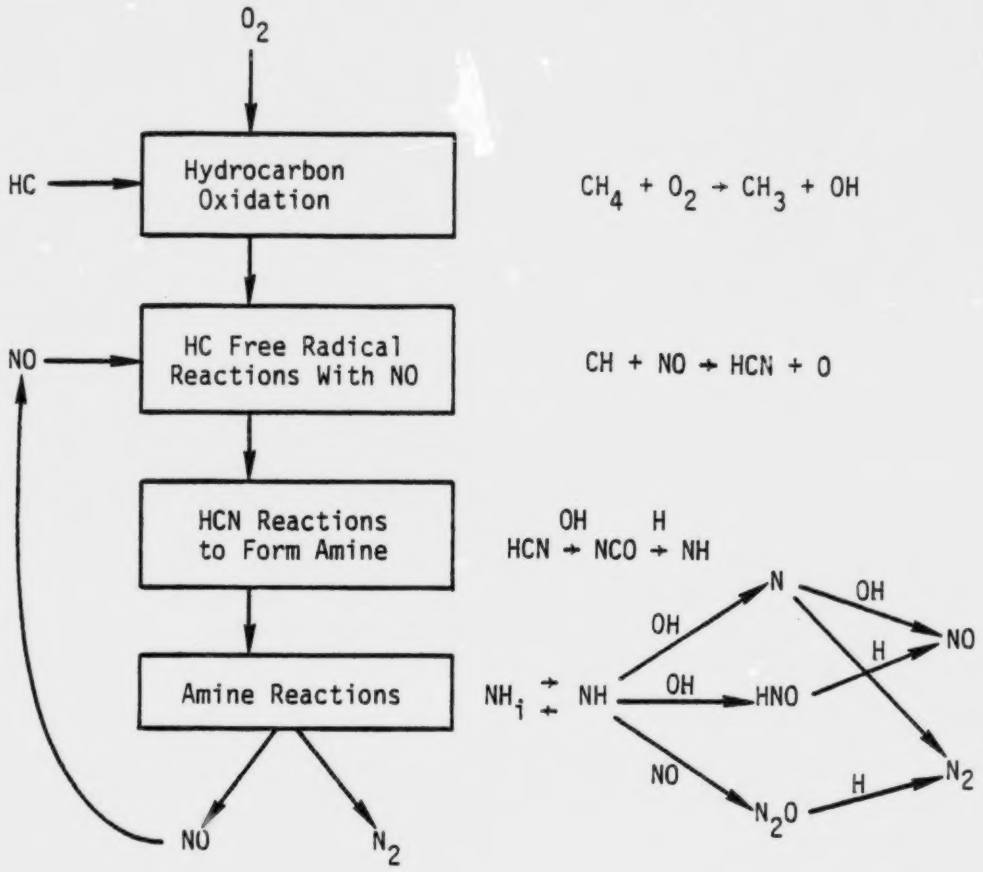

O_2
HC
Hydrocarbon Oxidation
$CH_4 + O_2 \rightarrow CH_3 + OH$
NO
HC Free Radical Reactions With NO
$CH + NO \rightarrow HCN + O$
HCN Reactions to Form Amine
$HCN \xrightarrow{OH} NCO \xrightarrow{H} NH$
Amine Reactions
$NH_i \rightleftarrows NH$
OH
N
OH
NO
OH
HNO
H
NO
N_2O
H
N_2
NO
N_2

Figure 2-4. Schematic of Gas-Phase Reactions Occurring During Reburning.

ibrium levels at higher temperature are significant except at very rich conditions. Such considerations have led to the development of advanced low-NO_x combustors for application to enhanced oil recovery steam generators and industrial boilers. These utilize high temperature precombustors which operate extremely rich in order to minimize fuel nitrogen conversion from burning heavy crude oils. For reburning, temperatures are expected to moderate (1500-1800°K), Therefore, just based upon equilibrium consideration (see Fig. 2-3), the optimum stoichiometry is expected to be between 0.9 and 1.0, which is in good agreement with gas-phase experimental data presented in the next section.

The initial NO level is expected to be of importance for two reasons: (1) it is the level that must be reduced and, (2) it influences the effectiveness of the reaction. The fast reactions, which contribute the largest overall reduction path, involve two fixed-nitrogen species; i.e., they are second-order reactions. For this reason, the effectiveness of the reduction reactions are expected to be less at lower concentrations of fixed nitrogen species. In other words, it is more difficult to get the same percent reduction at lower concentrations than was achievable at high concentrations.

One other gas-phase reaction consideration has been found to be important to the application of reburning technology. This is the formation of N_2O which may be favorable under some conditions of interest for reburning. In particular, under fuel-rich conditions a significant fraction of the intermediate amine species will react with NO to form N_2O. This represents a direct sink for NO. At higher temperatures N_2O is relatively unstable and will rapidly decompose to molecular nitrogen. However, there is evidence that temperature modification which can lower NO emission could result in the release of N_2O. Measurements using cryogenic sample concentration procedures developed at EER have shown significant increases in N_2O emissions from coal-fired bench-scale furnaces when cooling was added (Kramlich, et al., 1982). Because of potential degradation of the stratospheric ozone layer by N_2O, its emission may be of importance.

3.0 NO REDUCTION ZONE

The purpose of this section of the report is to examine fundamental processes occurring in the first step of the reburning process: the NO reduction zone. These data were obtained in a series of gas-phase laboratory experiments and bench-scale investigations with pulverized coal. Complete detailed descriptions of the experimental systems and raw data for each of the studies can be found in Appendices A and B, respectively.

The gas-phase experiments were carried out in the 2 kW back-fired reactor shown in Figure 3-1. A 5.71 cm ID alumina muffle tube separated the reaction zone from the propane/oxygen-enriched-air backfired zone. The reaction zone was divided into primary, NO reburning, and XN oxidation stages to simulate in-furnace NO_x reduction. Premixed primary reactants were introduced at the top of the reactor through a water-cooled, stainless-steel burner. Reburning fuel was injected radially outward at a position 2.29 cm downstream from the burner using a 1.27 cm OD quartz injector tube situated on the centerline of the reactor. Air was injected in a similar fashion 38 cm further downstream to combust the products from the NO reduction zone. Samples were withdrawn through a water-cooled, stainless steel probe situated 17.8 cm downstream of the injector.

The reburning investigations with pulverized coal were conducted at 20 kW in the refractory-lined tunnel furnace shown in Figure 3-2. This reactor has five separate sections, is 15.2 cm in internal diameter, and is 1.2 m long. The reburning fuels (primarily pulverized coals) were injected downstream of a radiation shield. The reburning fuels included propane, a lignite from Beulah, ND, a high-volatile bituminous coal from Utah, a medium-volatile coal from Rosa, AL, and a pre-dried Australian brown coal from Morwell (see Table 3-1 for properties). A staging choke separated the NO reduction zone from the burnout zone. Air to complete the combustion was supplied radially through an injection ring. Exhaust gas samples were withdrawn with a stainless-steel, water-jacketed probe and analyzed using standard continuous instrumentation. A water spray probe was used for extracting in-flame samples which were analyzed with specific ion electrodes for nitrogen intermediates.

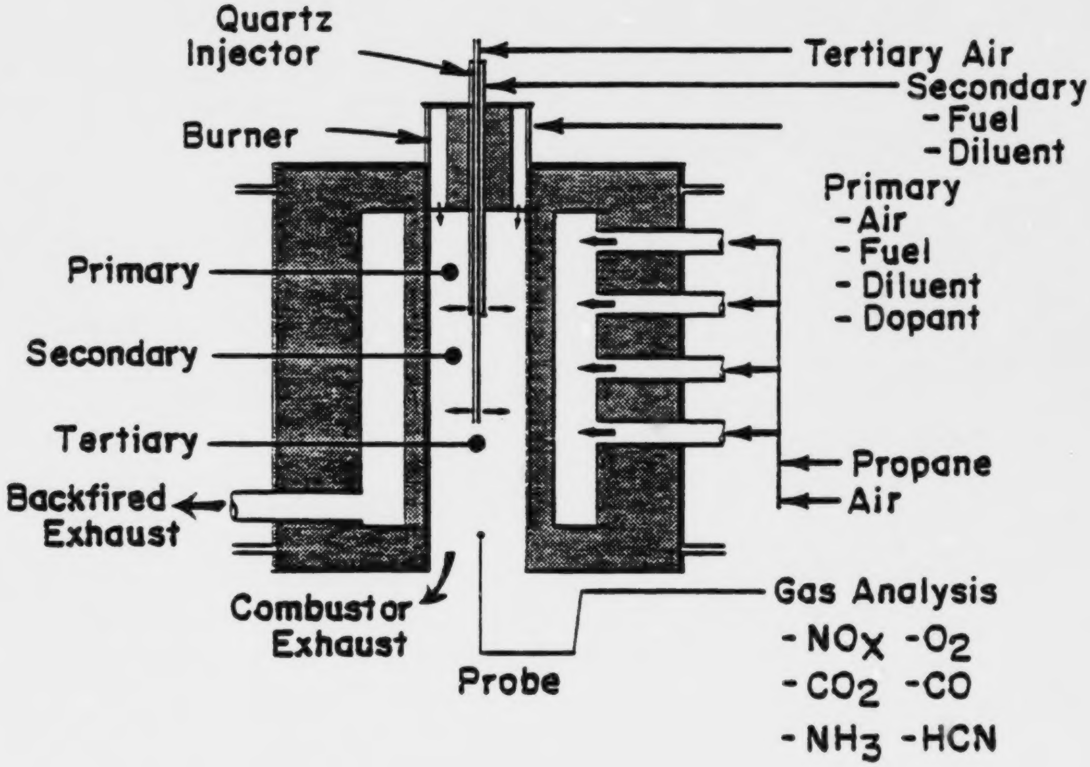

Quartz Injector
Tertiary Air
Secondary
- Fuel
- Diluent
Burner
Primary
- Air
- Fuel
- Diluent
- Dopant
Primary
Secondary
Tertiary
Propane
Air
Backfired Exhaust
Combustor Exhaust
Probe
Gas Analysis
- NOx - O2
- CO2 - CO
- NH3 - HCN

Figure 3-1. High Temperature Gas Fired Reactor With Back Heating.

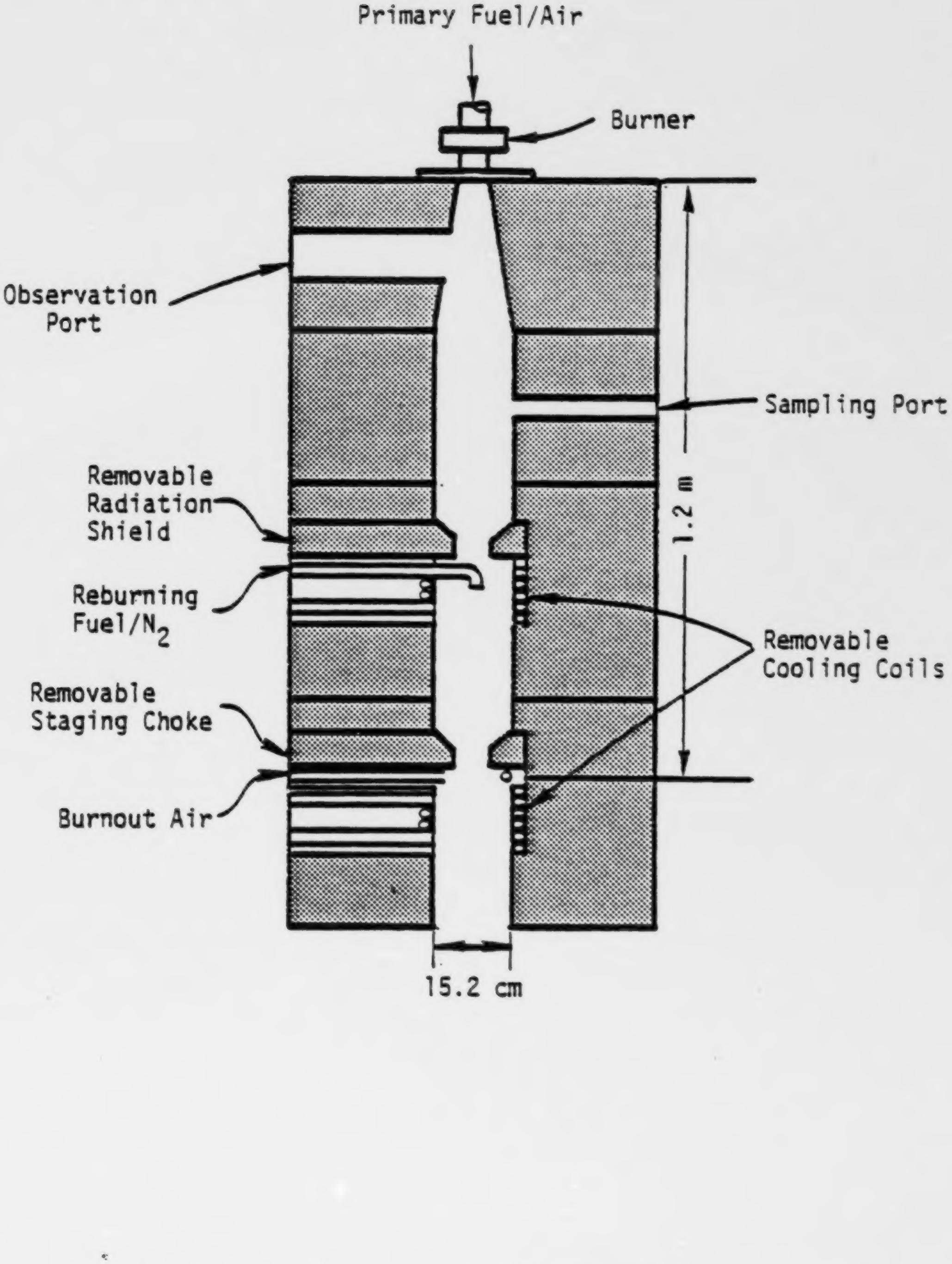

Primary Fuel/Air
Burner
Observation Port
Sampling Port
1.2 m
Removable Radiation Shield
Reburning Fuel/N_2
Removable Cooling Coils
Removable Staging Choke
Burnout Air
15.2 cm

Figure 3-2. Bench Scale Coal Fired System.

TABLE 3-1. COAL PROPERTIES

	UTAH	BEULAH	MORWELL	ROSA
Proximate Analysis (As Received)				
Moisture	6.39	34.63	9.07	8.02
Ash	7.40	4.97	3.38	6.79
Volatile Matter	38.89	27.02	48.79	21.81
Fixed Carbon	47.32	33.38	38.76	63.38
Ultimate Analysis (% Dry)				
Carbon	73.17	66.15	66.25	81.23
Hydrogen	5.55	4.20	5.01	4.73
Nitrogen	1.54	.96	0.65	1.74
Sulfur	.66	.37	0.28	1.04
Ash	7.90	7.60	3.72	7.38
Oxygen	11.18	20.72	24.09	3.88
Rank	HVB Bituminous	Lignite A	Predried Australian Brown Coal	MV Bituminous

3.1 Rich Zone Stoichiometry (SR_2)

3.1.1 Background Results

One of the most important parameters in the reburning process is the stoichiometry of the rich zone because it determines the amount of reburning fuel which must be used and controls the composition of the reactants entering the oxidizing stage. Figure 3-3 shows the data of Takahashi, et al. (1981), describing the influence of stoichiometry on the fraction of the NO which is decomposed in the rich zone. These results are reported in terms of the stoichiometry relative to the reburning fuel only:

$$\lambda = \frac{\text{moles } O_2 \text{ available at NO reduction zone inlet}}{\text{moles } O_2 \text{ required to completely burn the reburning fuel}}$$

These data suggest that for an air ratio, λ, between about 0.4 and 0.9, 90 percent of the NO is decomposed at 1300°C and 0.2 seconds. The data were obtained with a variety of fuels ranging from methane to kerosene and coal, and they indicate that the decomposition is not strongly dependent on the type of hydrocarbon fuel utilized (so long as it is high quality) and that the effectiveness of reburning decreases dramatically if the NO reduction zone is not fuel rich ($\lambda<1.0$). Figure 3-3 also visually suggests that reburning is not strongly sensitive to the rich zone stoichiometry below 1.0; however, when these data are replotted in terms of the more conventional second-stage stoichiometry (SR_2) the true importance of stoichiometry is more readily apparent. Throughout this report, all stoichiometric ratios are defined in terms of the total fuel input because this is consistent with the equilibrium on which the kinetic driving forces are based:

$$SR_2 = \frac{\text{moles } O_2 \text{ available at NO reduction zone inlet}}{\text{moles } O_2 \text{ required to burn primary + reburning fuel}}$$

Figure 3-4 shows the data of Takahashi, et al., replotted in this way. As the stoichiometry was reduced from 1.1, the exhaust NO_x decreased dramatically toward a minimum of approximately 42 percent of the initial value at SR_2=0.95. Further reductions in rich zone stoichiometry ultimately resulted in an increase in exhaust in all emissions.

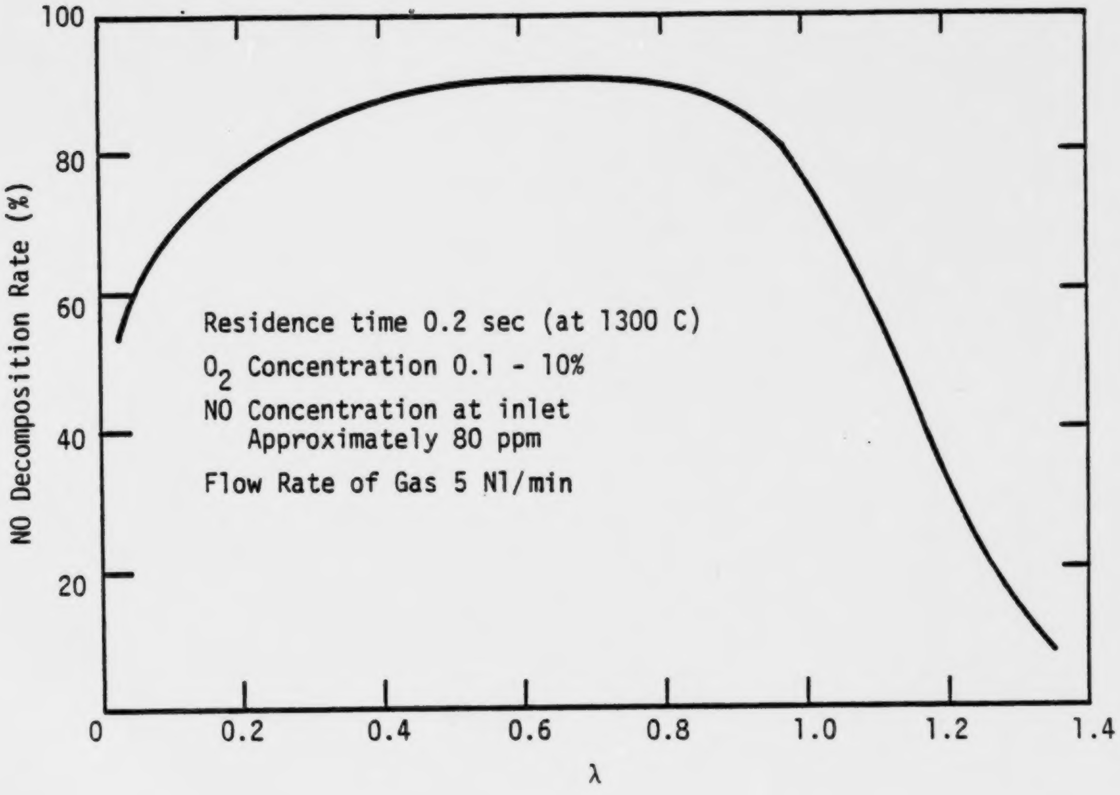
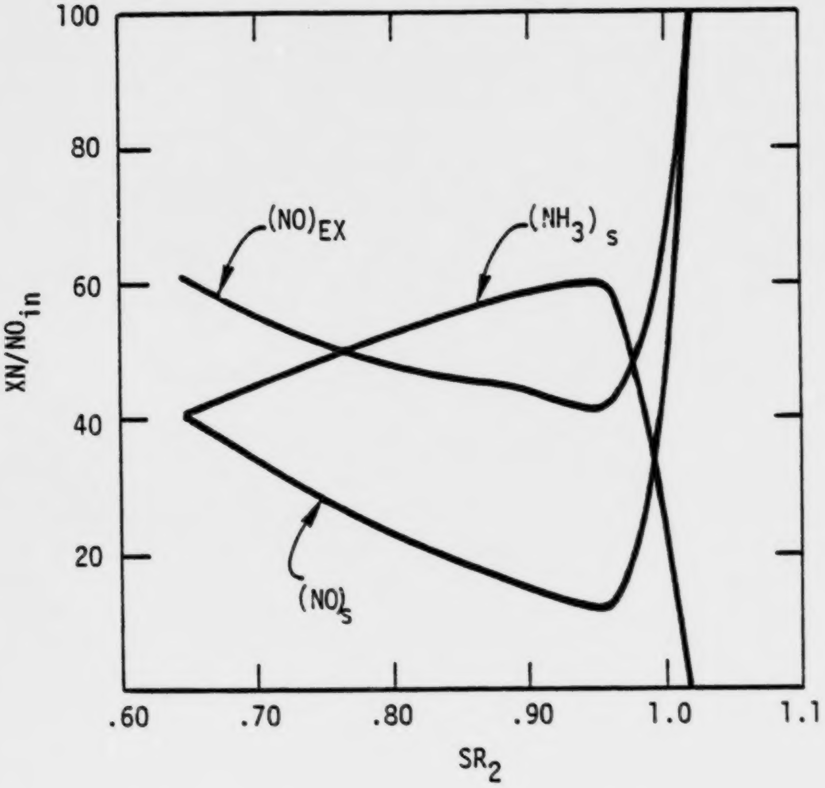


Figure 3-3. Influence of Air Ratio λ in DN Process on the NO Decomposition Rate for Various Fuels.



Takahashi, et al, Data

NO_{in} = 100 ppm

No Secondary Fuel N

T = 1300 C

Figure 3-4. Influence of NO Reduction Zone Stoichiometry on Nitrogen Speciation and Exhaust NO. (Replotted from Data of Takahashi, et al, 1981.)

3.1.2 Gas-Phase Studies--Laboratory Reactor

Figure 3-5 shows the results of similar tests in the back-fired reactor with two levels of secondary fuel nitrogen. At the optimum secondary stoichiometry (around 90 percent theoretical air) approximately half of the NO was removed by reburning regardless of the secondary fuel nitrogen content. The tertiary to primary NO ratio at richer secondary stoichiometries increased more rapidly when fuel nitrogen was present in the secondary due to the increased ratio of secondary to primary fuel, suggesting that the nitrogen content of the reburning fuel may be of major importance if the reburning system is not fully optimized. Figure 3-6 shows the fixed nitrogen XN levels in the secondary under the same conditions. The open data points and solid lines indicate the data obtained with the nitrogen-free reburning fuel; the shaded points and dotted lines indicate the presence of 0.5 percent ammonia in the secondary fuel. In general, the secondary NO levels do not appear to be greatly influenced by the presence of the fuel nitrogen in the rich zone; in both cases the NO dropped off sharply as secondary stoichiometry became richer. These data suggest that the presence of nitrogen in the reburning fuel does not greatly retard the destruction of primary NO. However, as the stoichiometry is further reduced, the decrease in primary NO is offset by a corresponding rise in HCN, the dominant fixed nitrogen species at rich secondary stoichiometries. Secondary HCN levels were approximately 50 percent higher when fuel nitrogen was included with the reburning fuel.

Figures 3-7 and 3-8 show the relative fuel nitrogen levels in each of the three stages. These data are reported relative to the NO concentration at the primary exit (corrected for dilution effects due to added mass of secondary and tertiary). The open hexagons are the total fixed nitrogen (NO + NH_3 + HCN) in the secondary exit stream and the solid points represent the exhaust NO concentrations. Occasionally NO_2 measurements were taken in the tertiary and in the primary; the concentrations of this species were always negligible. When fuel nitrogen was not included in the reburning fuel (Figure 3-7) the difference between the primary NO and the secondary TFN was greater than the difference between the secondary TFN and the tertiary NO indicating that most of the reduction in fixed nitrogen occurred in the fuel rich zone. The minimum in secondary TFN occurred at approximately 80 percent theoretical air, whereas the minimum in exhaust NO occurred at a leaner

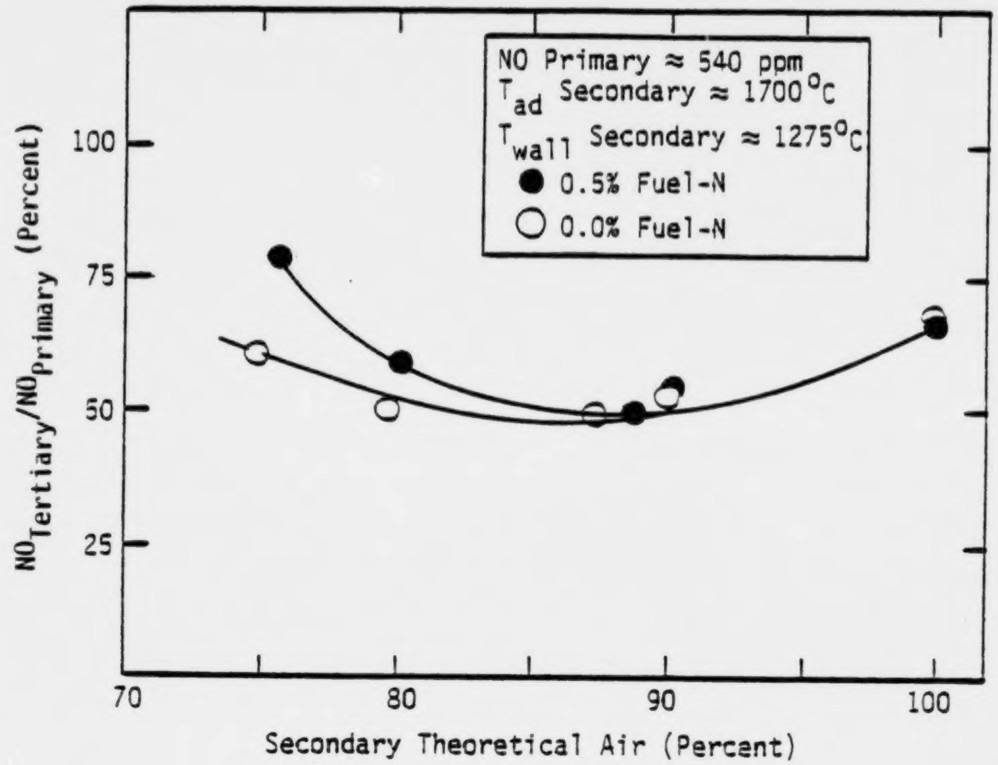


Figure 3-5. Effect of NO Reduction Zone Stoichiometry on Gas Phase Reduction of NO. (Gas Phase Back-Fired Reactor with CH_4 Reburning Fuel.)

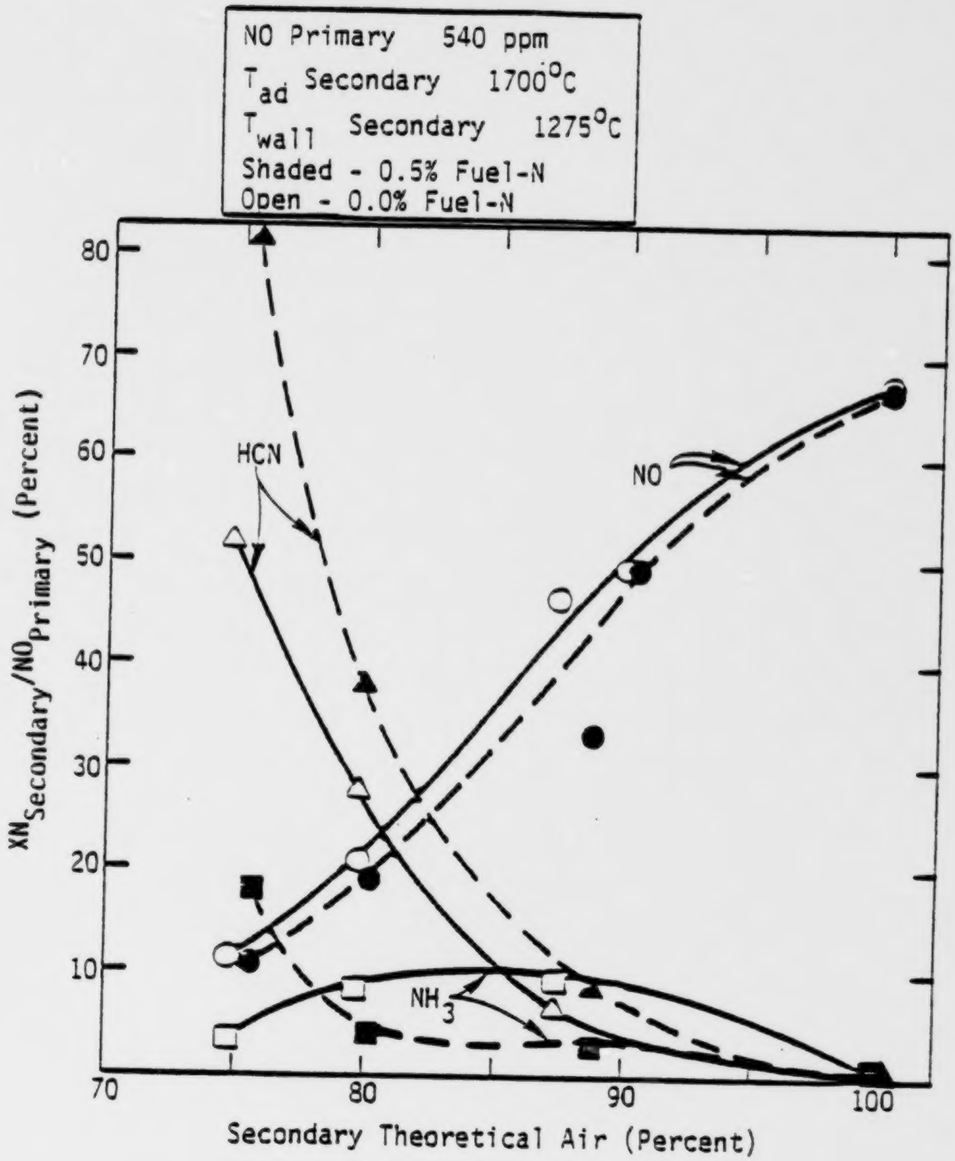


Figure 3-6. Nitrogen Speciation as a Function of NO Reduction Zone Stoichiometry in Back-Fired Reactor (CH_4 Reburning Fuel).

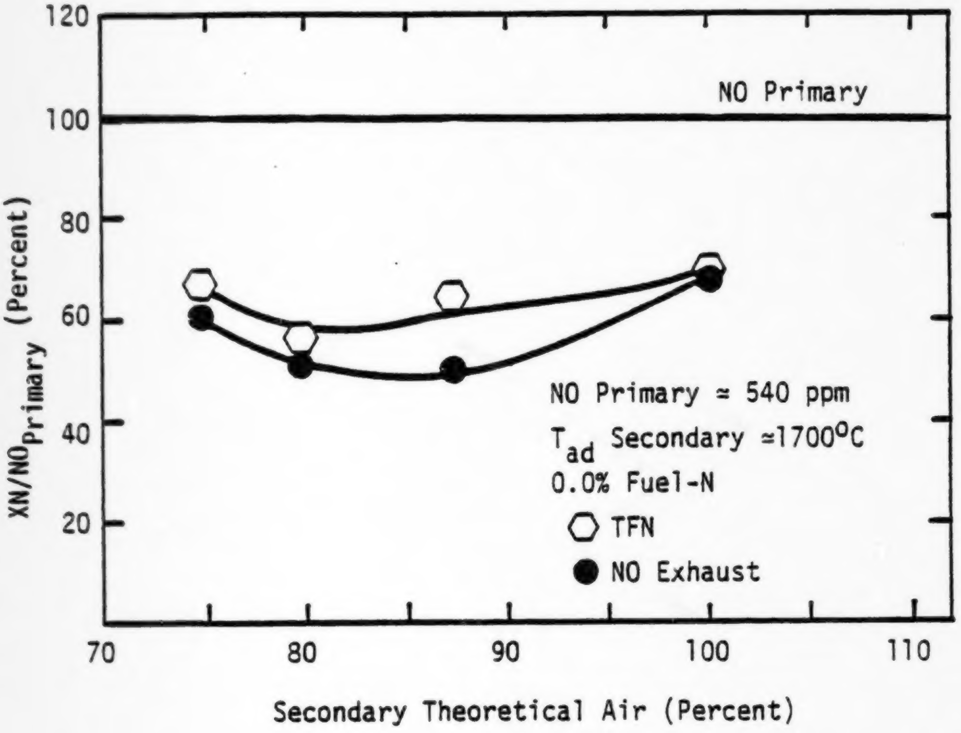


Figure 3-7. The Conversion of NO Primary to TFN and Exhaust NO (CH_4/N_2 as the Reburning Fuel in Backfired Reactor).

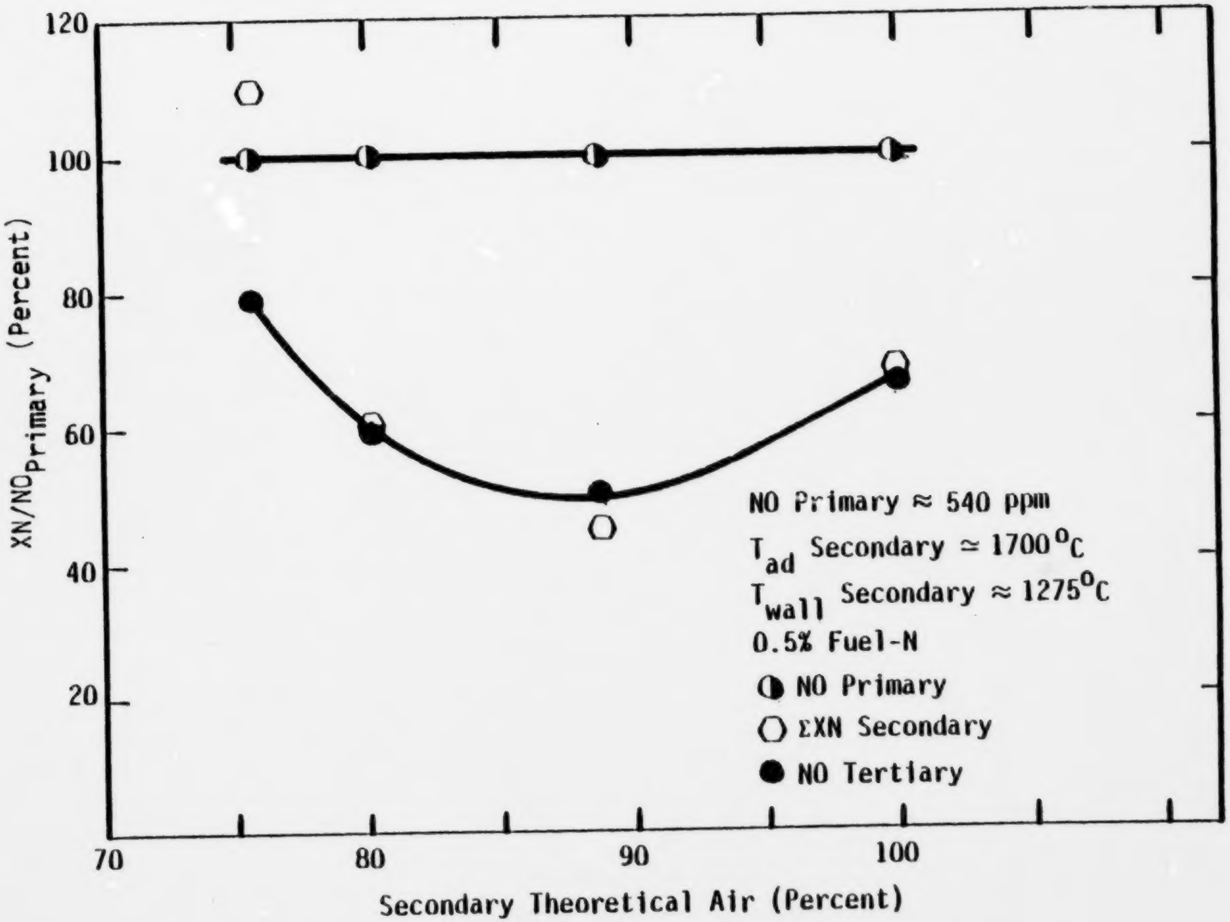


Figure 3-8. The Conversion of NO Primary to TFN and Exhaust NO ($CH_4/NH_3/N_2$ as the Reburning Fuel in Backfired Reactor).

stoichiometry corresponding to the peak in secondary NH_3 (Figure 3-6). These data emphasize that to optimize the reburning concept it is necessary to collectively optimize both the NO reduction step and the XN oxidation step. The data also suggest that secondary NH_3 formation in the secondary stage may contribute to NO reduction in the tertiary stage. Figure 3-8 shows that when the reburning fuel contained fuel nitrogen essentially all of the NO reduction occurred in the first stage at all but the richest secondary stoichiometry.

3.1.3 Bench-Scale Results

Figure 3-9 shows similar results obtained in the tunnel furnace. In these experiments, the main fuel was propane-doped with NO to 633 ppm (in the primary zone exhaust) and the remaining fuel was the Beulah lignite. Again the data are reported in terms of the dilution corrected ratio of NO in the furnace exhaust to NO at the exit of the primary zone in percent. In these experiments, both the primary stoichiometry and the tertiary stoichiometry were maintained at 1.1 and 1.25, respectively. Figure 3-9 also shows data obtained under similar conditions with propane as the reburning fuel (containing no fuel nitrogen). At the optimum secondary zone stoichiometry of approximately 0.9, the exhaust emissions were near 50 percent of the emissions without reburning and this is in good agreement with the work of Takahashi, et al. (1981), and Clark, et al. (1982). As the secondary zone stoichiometry is reduced, the amount of reburning fuel required increases. If the reburning fuel is heavy oil or coal, and contains significant fuel nitrogen, then the reactive nitrogen content of the rich zone also increases. When the Beulah coal was used as the reburning fuel, the effectiveness of the reburning decreased dramatically as the rich zone stoichiometry was reduced below 0.9, while with the propane as the reburning fuel, only a moderate decrease in effectiveness was observed. The difference is believed to be directly attributable to the fuel nitrogen contained in the Beulah coal.

Figure 3-10 shows the results of gas-phase concentration measurements made at the end of the secondary zone (fuel rich). The purpose of the NO reduction zone is to react nitric oxide leaving the first stage with hydrocarbon radicals by reactions such as:

$$NO + CH \rightarrow N + CHO$$

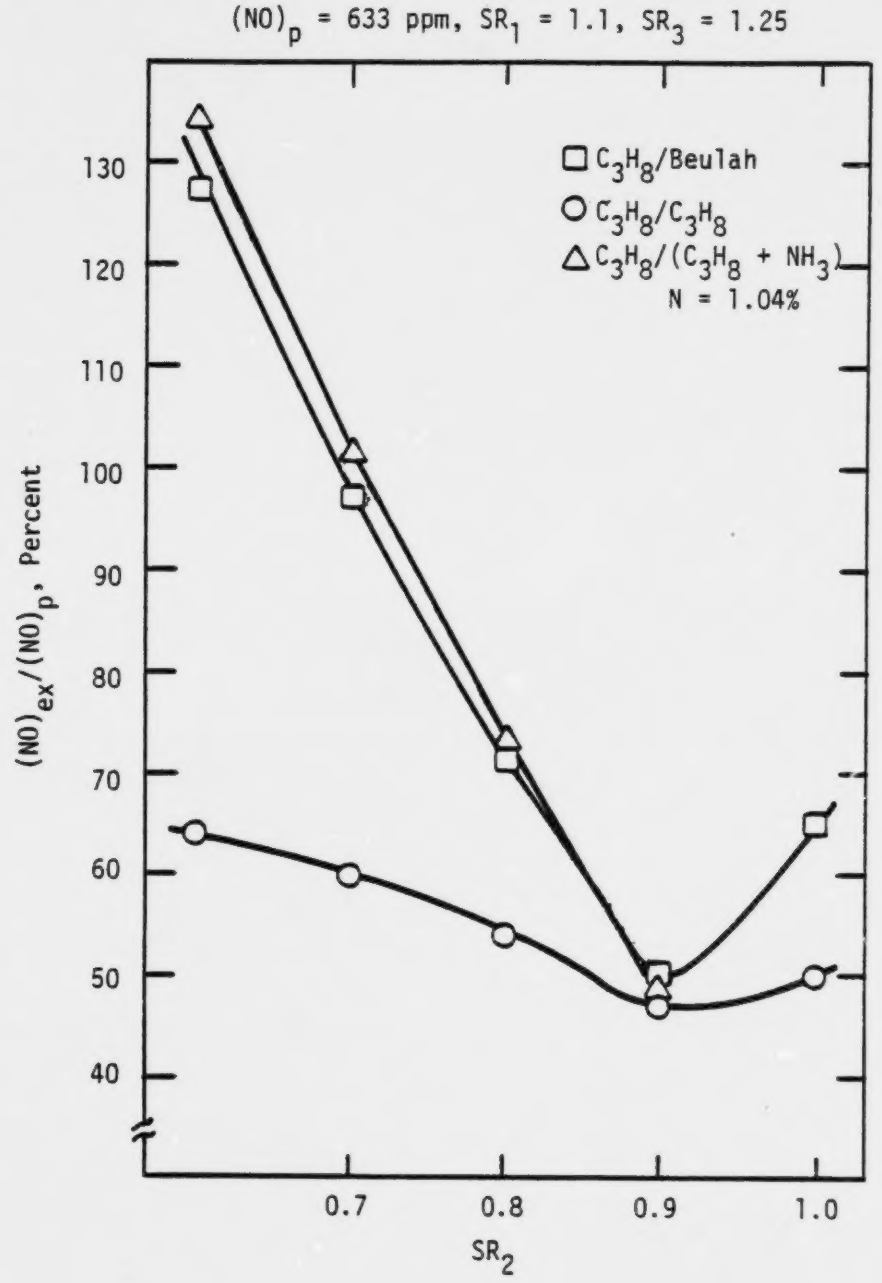


Figure 3-9. Typical Tunnel Furnace Results on the Influence of SR_2.

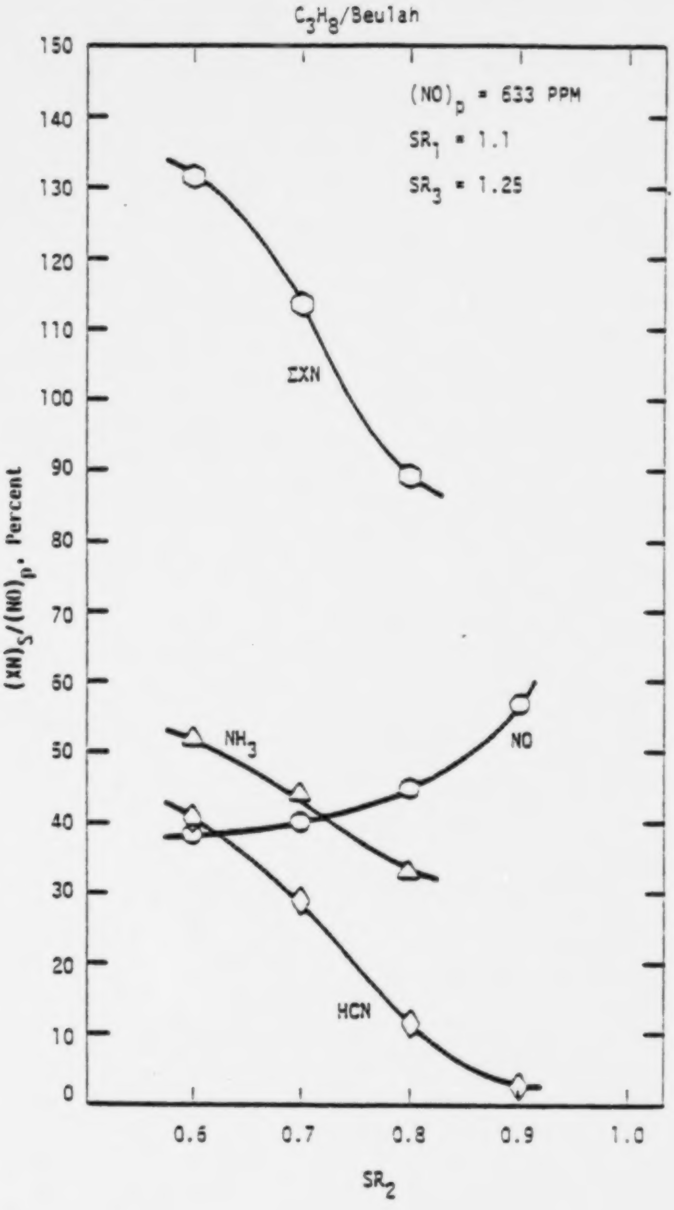


Figure 3-10. Gas Phase Species Concentrations at the Second-Stage Exit of the Tunnel Furnace (C_3H_8/Beulah)

and

$$NO + CH \rightarrow HCN + O$$

Figure 3-10 indicates that this type of reduction is occurring at all rich-zone stoichiometries as expected. In addition, there appears to be considerable interconversion of nitrogen among different fixed nitrogen species. At second stage stoichiometries below 0.8, NH_3 and HCN formation becomes significant. Further, these data demonstrate that as the secondary zone stoichiometry is reduced, the summation of the XN species increases dramatically. Figure 3-11 shows these same data replotted with the XN species concentrations normalized with respect to the total available reactive nitrogen in the rich zone (the NO exiting the primary zone plus the nitrogen in the coal). Figure 3-11 demonstrates that although the NO leaving the secondary zone decreases dramatically as SR_2 is reduced, the TFN remains approximately 30 percent of the total available nitrogen. Therefore, decreasing the secondary stoichiometry (by adding more reburning fuel) results in higher exhaust NO_x partially because it increases the available reactive nitrogen. Additionally, as in the case of the back-fired reactor gas data (Figure 3-6) and in the case of the Takahashi data (Figure 3-4), the NH_3 appears to peak near the minimum in exhaust NO_x and then decay as SR_2 is further reduced.

Figure 3-12 summarizes the fate of the available nitrogen on a cumulative basis and includes consideration of the char nitrogen. These results emphasize that at low secondary zone stoichiometries, char nitrogen carry-over (into the oxygen-rich third stage) can be extremely significant. When the secondary zone stoichiometry is decreased from 0.9 to 0.7 the amount of reburning fuel nitrogen input to the system approximately doubles, yet the char nitrogen carry-over increases from the equivalent of approximately 40 percent of the initial NO level to almost 150 percent of the initial NO level. Additionally, the fraction of the available reactive nitrogen which is converted to N_2 in the rich stage decreases significantly as SR_2 is decreased.

3.2 Primary Zone Stoichiometry

Figure 3-13 shows kinetic calculations on the fraction of the NO remaining at the exit of the second stage as a function of the primary zone oxygen. These results suggest that increasing the oxygen concentration of the gases entering the fuel-rich stage (for a constant SR_2) should decrease the amount

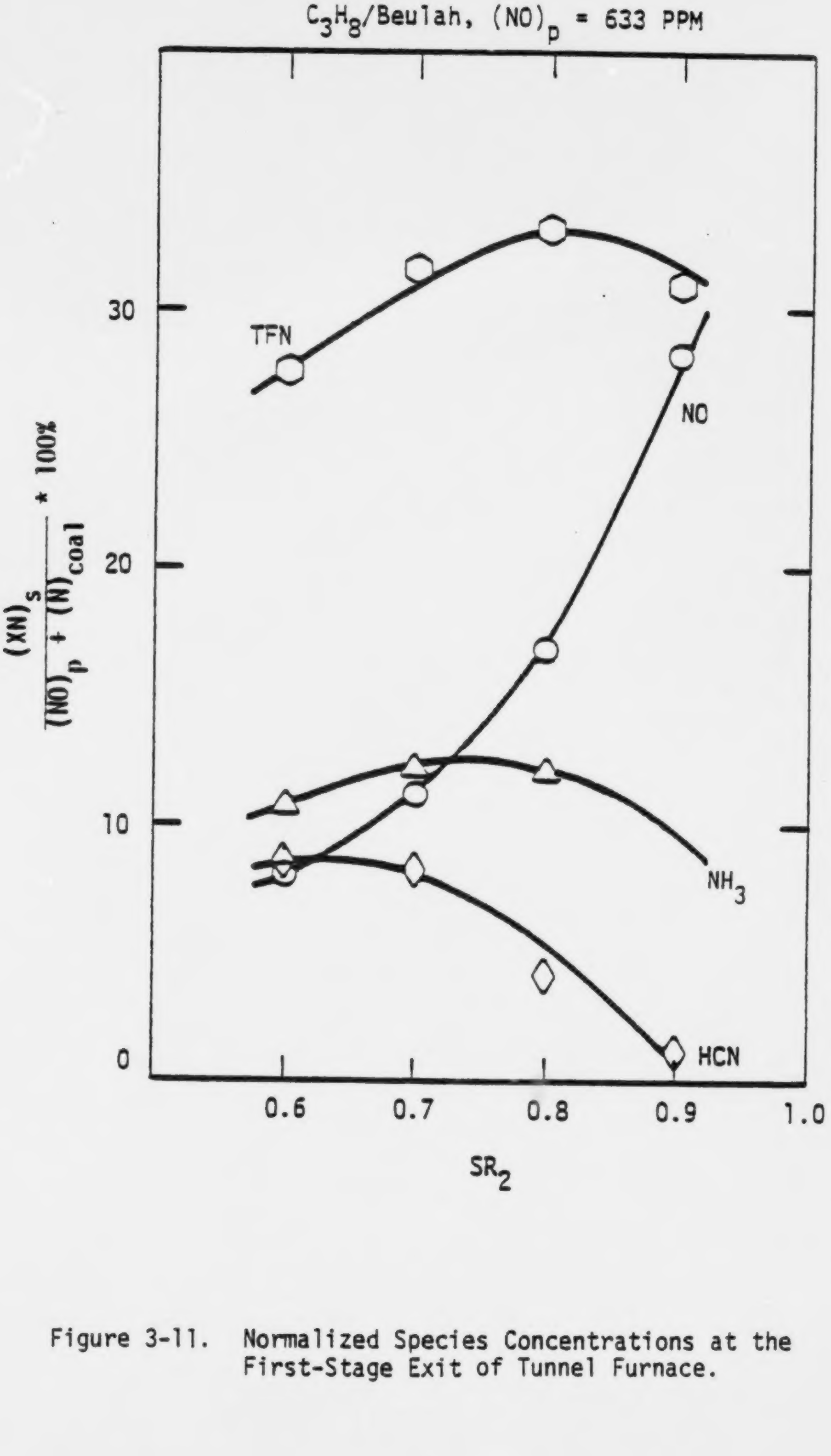


Figure 3-11. Normalized Species Concentrations at the First-Stage Exit of Tunnel Furnace.

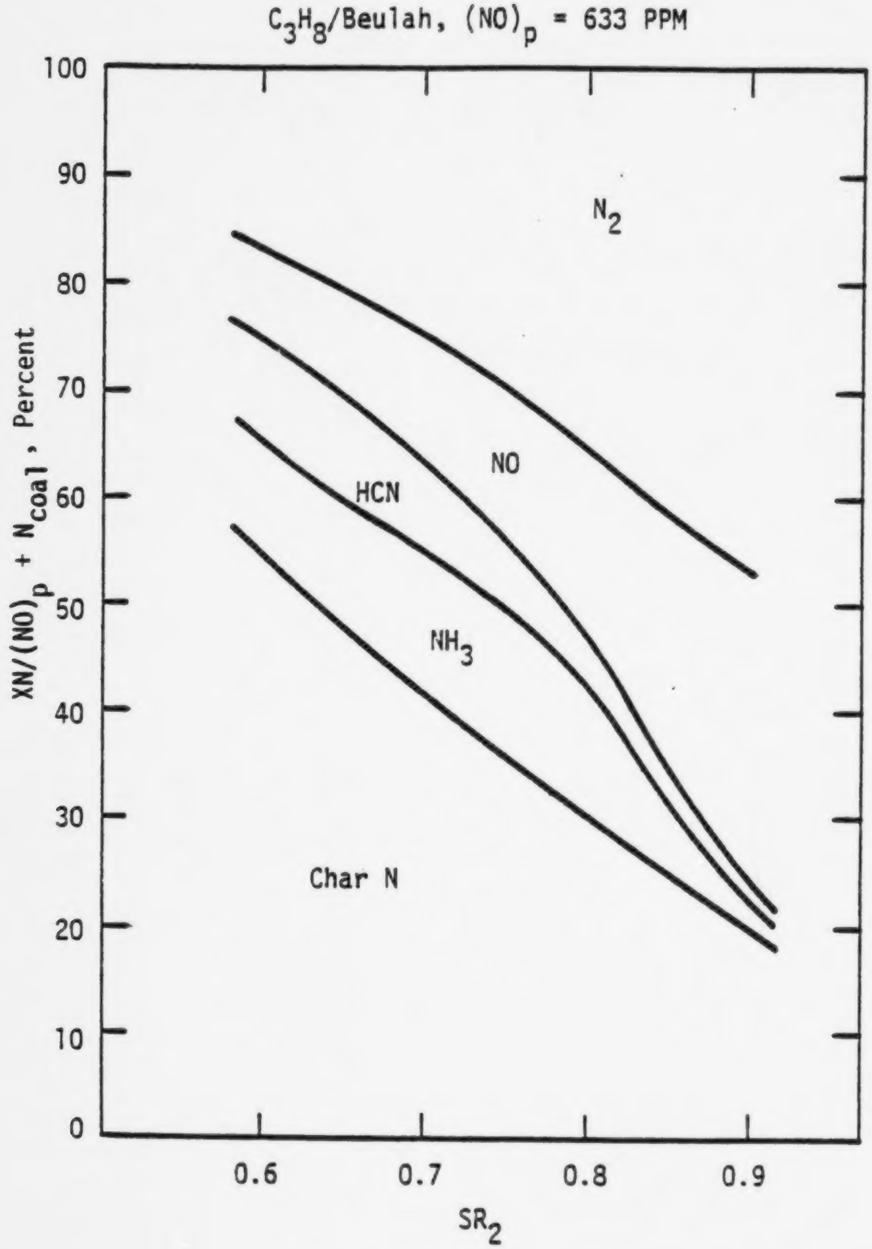


Figure 3-12. Fate of First-Stage NO and Coal Nitrogen, Second-Stage Exit of Tunnel Furnace.

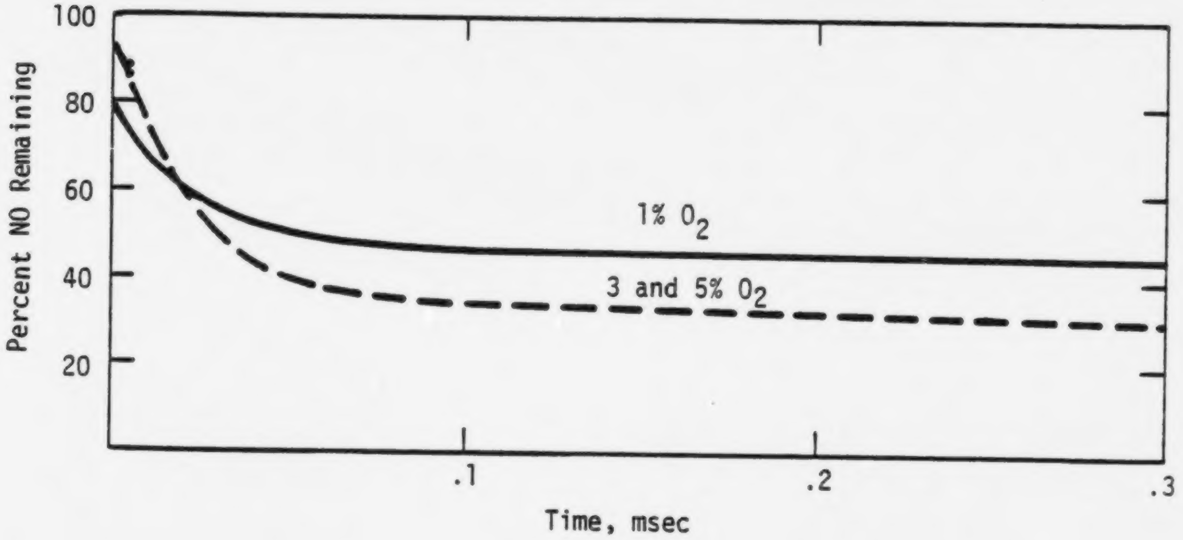


Figure 3-13. Analytical Calculations on the Effect of Residence Time and Primary Zone Oxygen on NO Reduction by Reburning (FCR Kinetic Set).

of NO remaining at the exit of the fuel-rich stage. Examination of the kinetic output indicates that this effect is primarily associated with the increased combustion; increased excess O_2 necessitates increased fuel addition to maintain a constant SR_2. Figure 3-14 shows tunnel furnace results obtained with the propane/Utah system as a function of the primary zone stoichiometry. These data indicate that as the primary zone excess oxygen is increased, the exhaust NO_x also increases. Increasing SR_1 does increase the rich zone combustion as predicted by the kinetic model; however, with a real solid fuel, it also increases the amount of reburning fuel nitrogen which enters the reacting system. Figure 3-15 shows the total available reactive nitrogen (primary NO plus nitrogen in the reburning coal) as a function of SR_1. Figure 3-15 also indicates that as the primary zone stoichiometry is increased the conversion of the available nitrogen decreases. This is almost certainly due to the increased combustion and to the fact that the relative conversion of the coal nitrogen is less than that of the primary zone NO. The overall sum of the two effects (Figure 3-14) is only a slight increase in exhaust NO_x at the optimum conditions. However, in a large-scale system increasing SR_1 could be more detrimental to the reburning effectives because it will not be possible to maintain a uniform rich-zone stoichiometry (SR_2) at the optimum value. Further, from a practical point of view, it is not desirable to operate the primary zone at high excess O_2 levels because this will increase the fuel requirements in the reburning zone.

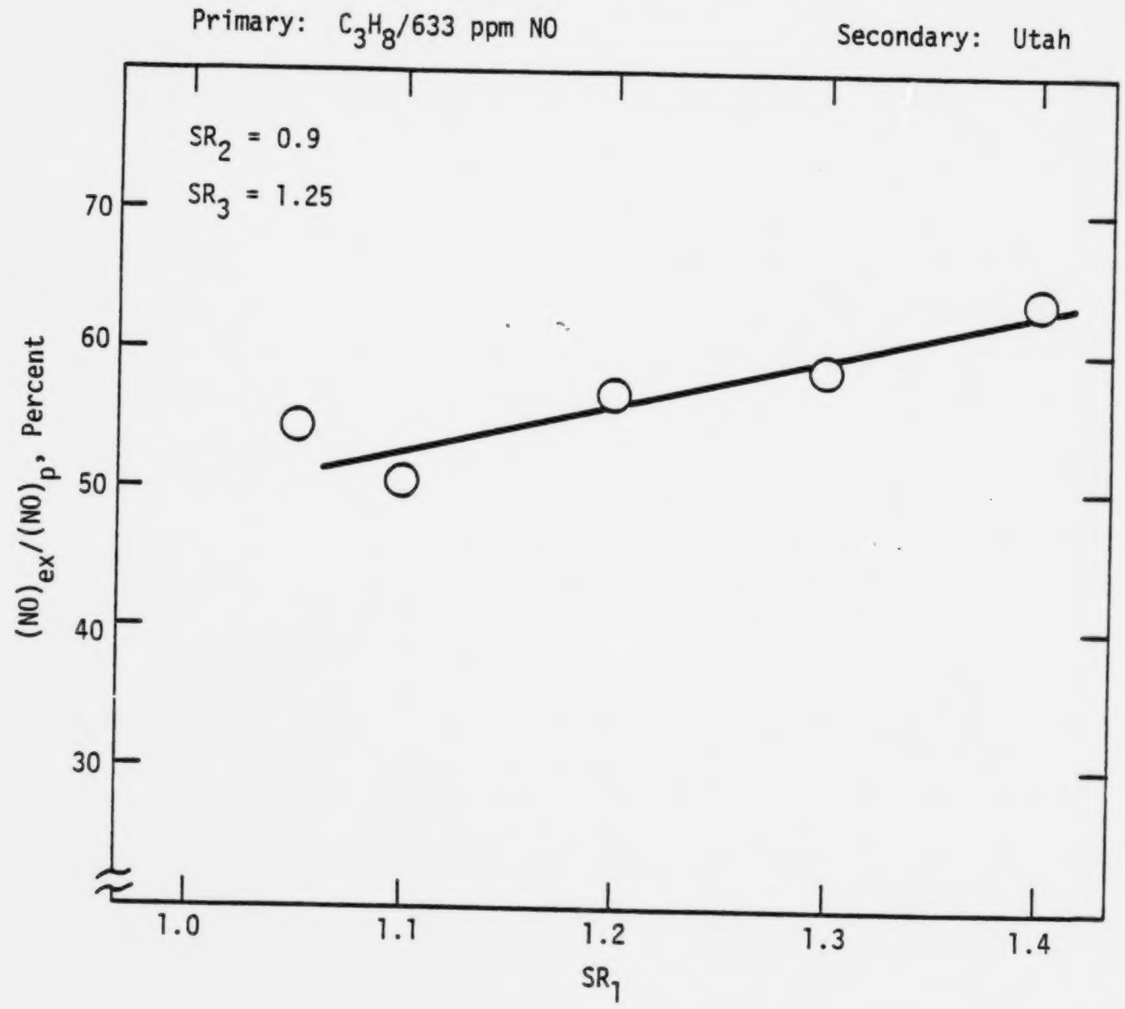


Figure 3-14. Influence of Primary Zone Stoichiometry on NO Reduction by Reburning with Beulah Lignite in Tunnel Furnace.

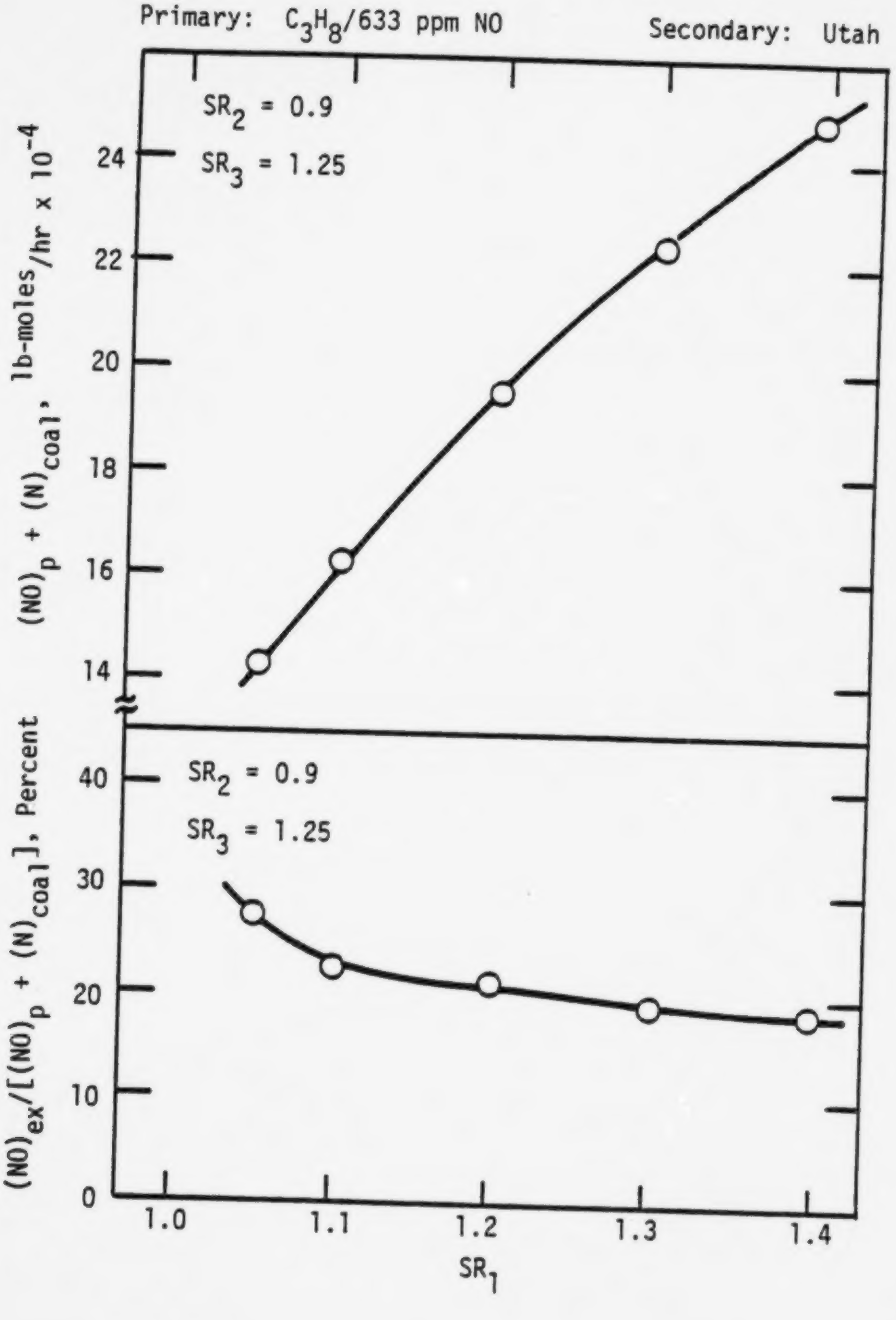


Figure 3-15. Effect of Primary Zone Stoichiometry on Amount of Nitrogen Addition and Reburning Efficiency.

4.0 XN OXIDATION ZONE

4.1 Overall XN to NO Conversion

Figure 4-1 shows typical results obtained with the propane/Beulah system in the tunnel furnace to define the fate of the nitrogen species in a reburning system. As discussed previously, when the rich-zone stoichiometry is reduced, the amount of reburning fuel increases and the amount of reactive material being carried into the XN oxidation zone (third stage) increases dramatically. As Figure 4-1 indicates at SR_2 equals 0.9, the total available nitrogen at the end of the second stage (TXN = NO + NH_3 + HCN + char N) is approximately equivalent to the primary NO. However, by SR_2 equals 0.7 the TXN has increased to almost 2.5 times the initial NO level. Fortunately, the conversion of this material to NO decreases as the TXN level increases. This is due to the increased importance of char nitrogen (which has a lower conversion) and to the second-order nature of the N_2 formation reactions. Nonetheless, as the TXN level increases, so do the exhaust NO emissions. Thus, it is important to understand the influence of the combustion parameters on the oxidation of the TXN species in the third stage. In order to optimize the reburning concept it is necessary to both maximize the destruction of NO in the rich zone and minimize the oxidation of the remaining TXN species in the third stage of the system.

4.2 Tertiary Zone Stoichiometry (SR_3)

Figure 4-2 shows the influence of the final zone stoichiometry for a constant primary stoichiometry of 1.1 and secondary stoichiometry of 0.9 in the tunnel furnace with the Utah coal as the reburning fuel. As expected, the overall stoichiometry had little influence on the exhaust NO emissions. A 55 percent reduction in emissions was achieved in this reburning configuration for all of the overall stoichiometries studied. These data agree with those obtained by Chen et al. (1982), which indicated that in staged combustion systems, the stoichiometry of the final zone has little influence on exhaust NO_x emissions.

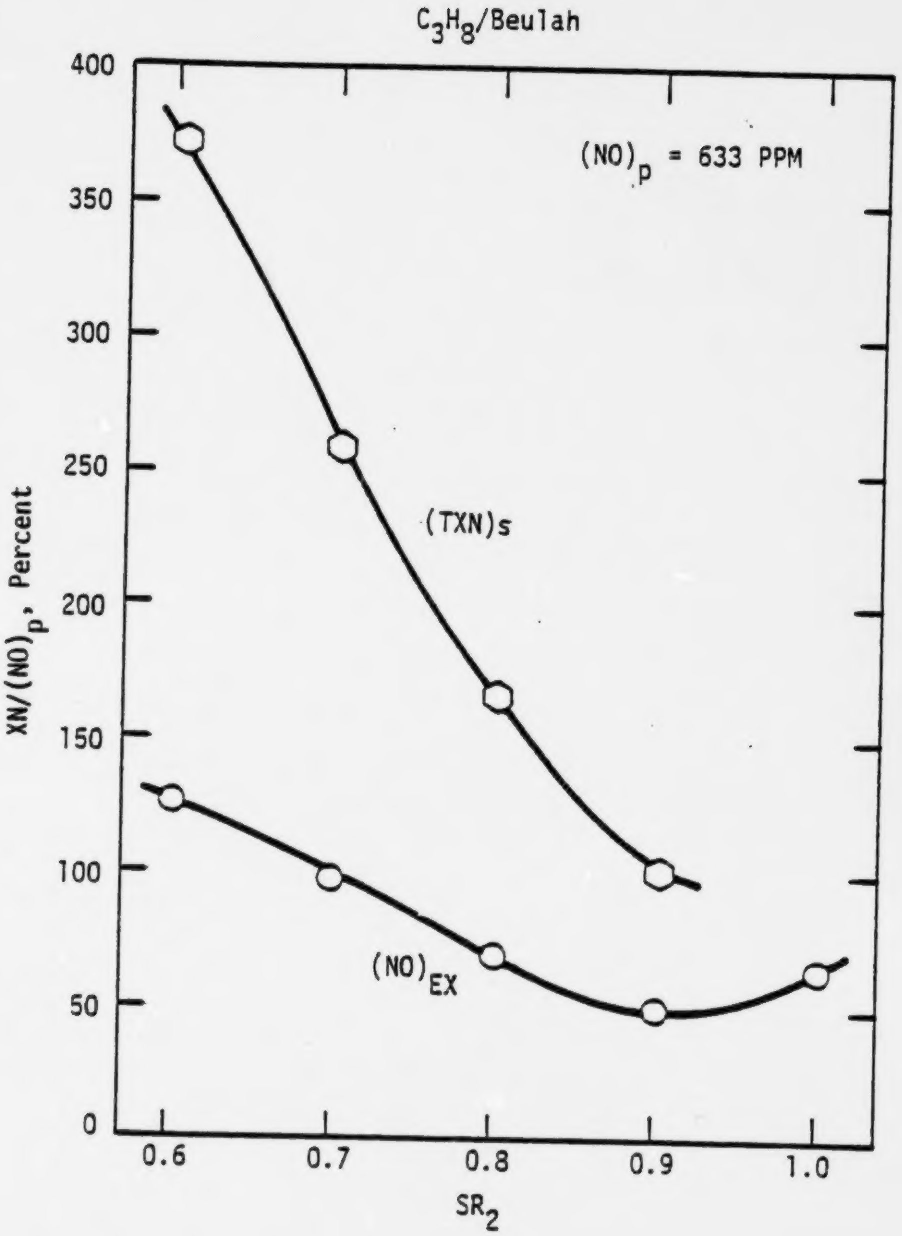


Figure 4-1. TXN Oxidation in the Third Stage (XN Oxidation Zone) of Tunnel Furnace.

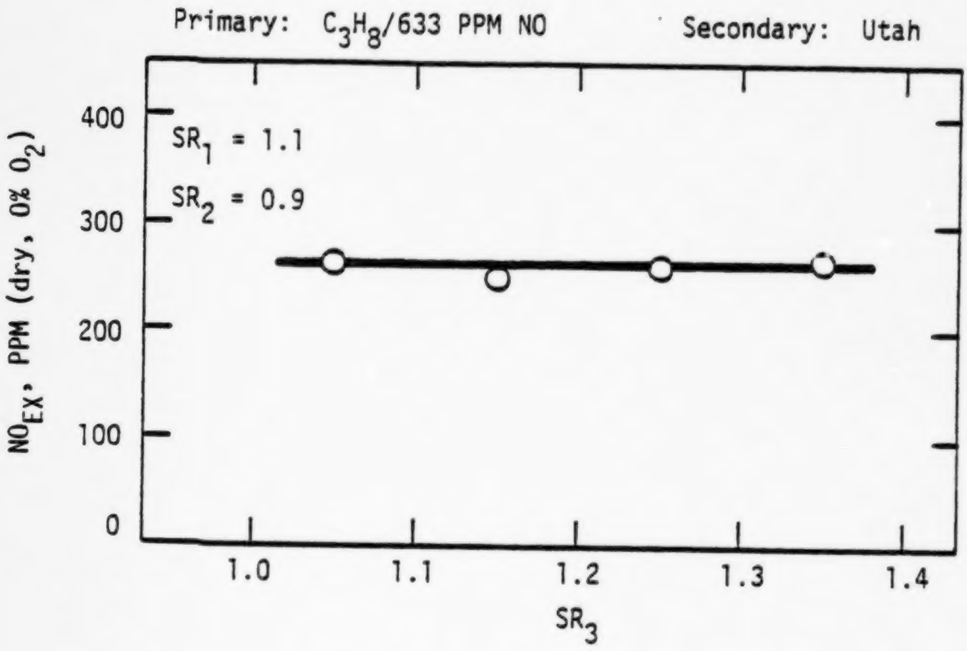


Figure 4-2. Effect of Tertiary (Overall) Stoichiometry on NO Emissions.

5.0 IMPORTANCE OF FIELD APPLICATION CONSTRAINTS

The purpose of this section of the report is to examine the influence of fuel parameters which may influence the effectiveness of the concept in actual, full-scale applications. This is particularly significant because almost all of the early work (Wendt, et al., 1973 and Takahashi, et al., 1981) was conducted with reburning fuels which were nitrogen free.

5.1 Nitrogen Content of the Reburning Fuel

Figure 5-1 shows limited results obtained by Takahashi on doped liquid fuels firing at 40 to 55 percent load. These data indicate that the NO_x emissions increased significantly with increasing fuel nitrogen content (due to increased primary NO levels); however, the reburning effectiveness appears to be relatively independent of the fuel oil nitrogen content. (It should be further emphasized that these data were obtained by doping a medium weight fuel oil with a very light nitrogen compound, pyridine.)

The influence of fuel nitrogen content was investigated in the back-fired bench-scale reactor by varying the proportion of ammonia in the secondary fuel. Figure 5-2 shows that when a high NO_x combustion gas was reburned at a stoichiometry of 90 percent theoretical air, the tertiary to primary NO ratio increased only slightly with increasing reburning fuel nitrogen content between 0.19 and 1.07 percent N (NH_3 to primary NO ratios between 1 and 6). Even for the high-nitrogen fuel, tertiary NO emissions were only marginally increased in the presence of secondary fuel nitrogen. These results indicate that the nitrogen content of the reburning fuel has relatively little influence on the reburning effectiveness under optimum combustion conditions with gaseous fuels.

Figure 5-3 shows the results from a series of carefully controlled tests in the tunnel furnace where the fuel nitrogen content of the reburning fuel was varied from 0 to 1.67 weight percent nitrogen as NH_3. (The uneven values of nitrogen content correspond directly to the coals which were also tested.) In all of these experiments the primary zone fuel was also propane and the initial NO was 633 ppm. These data indicate that, as previously noted, the optimum NO reduction-zone stoichiometry is approximately 0.9 and that further decreases ultimately result in decreased reburning efficiency. These data also show that under optimum reburning conditions, fuel nitrogen content has

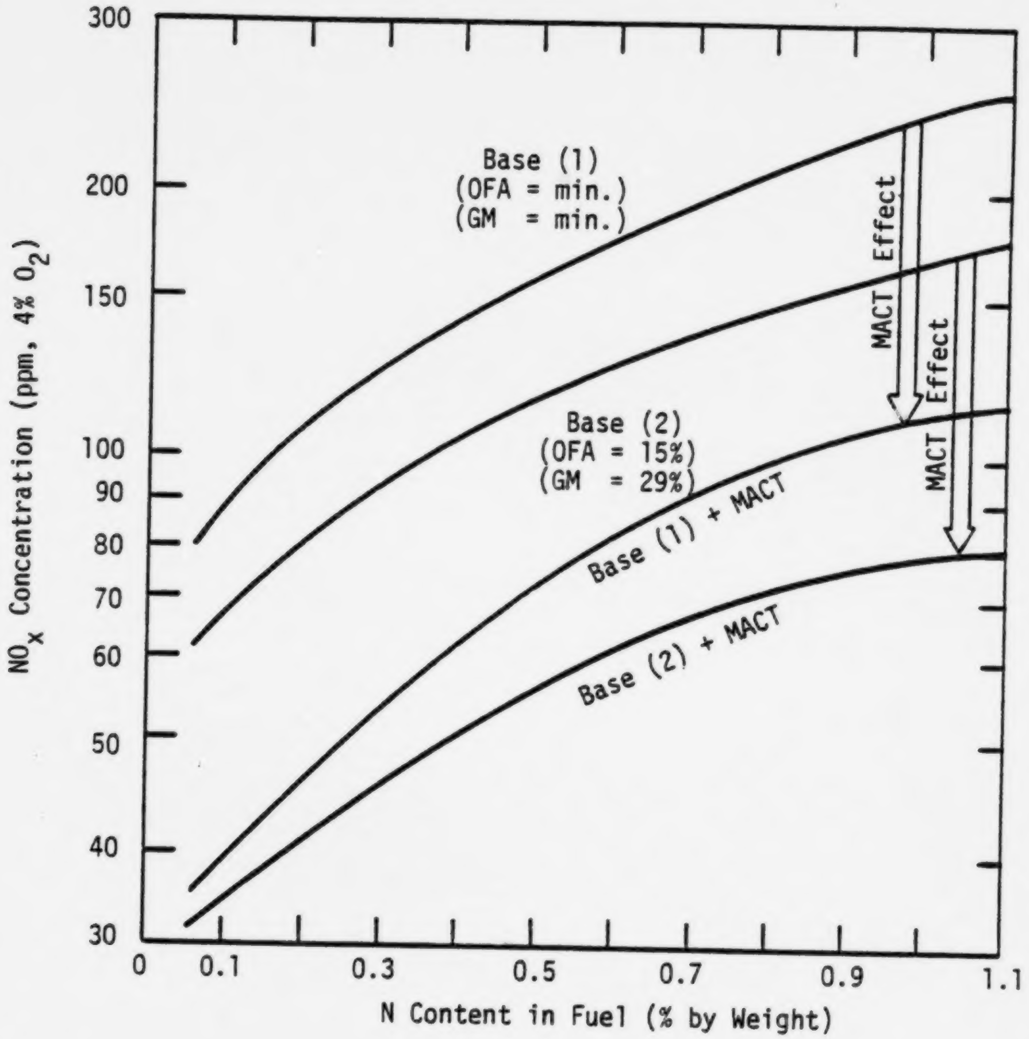


Figure 5-1. Dependence of NO_x Concentration on the Nitrogen Content in Heavy Fuel Oil.

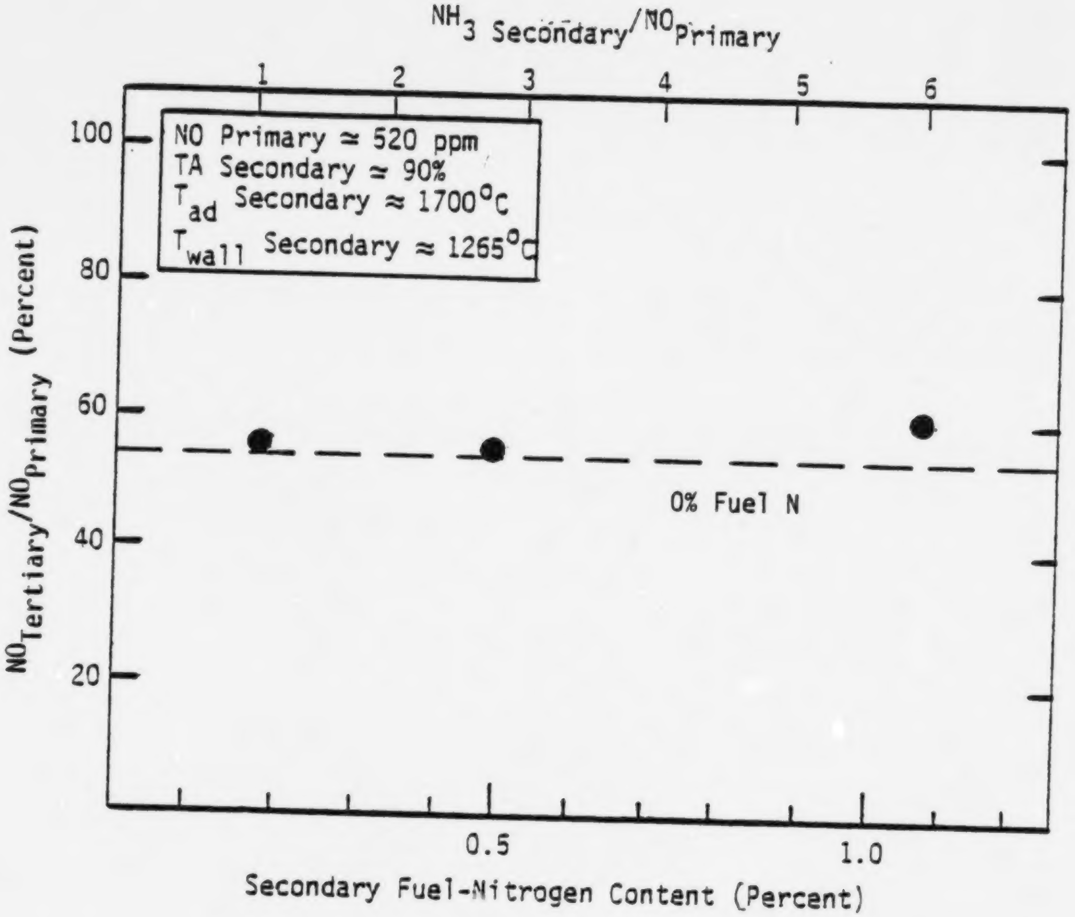


Figure 5-2. Influence of Fuel Nitrogen Content of Reburning Fuel for High Primary NO Condition (Back Fired Reactor).

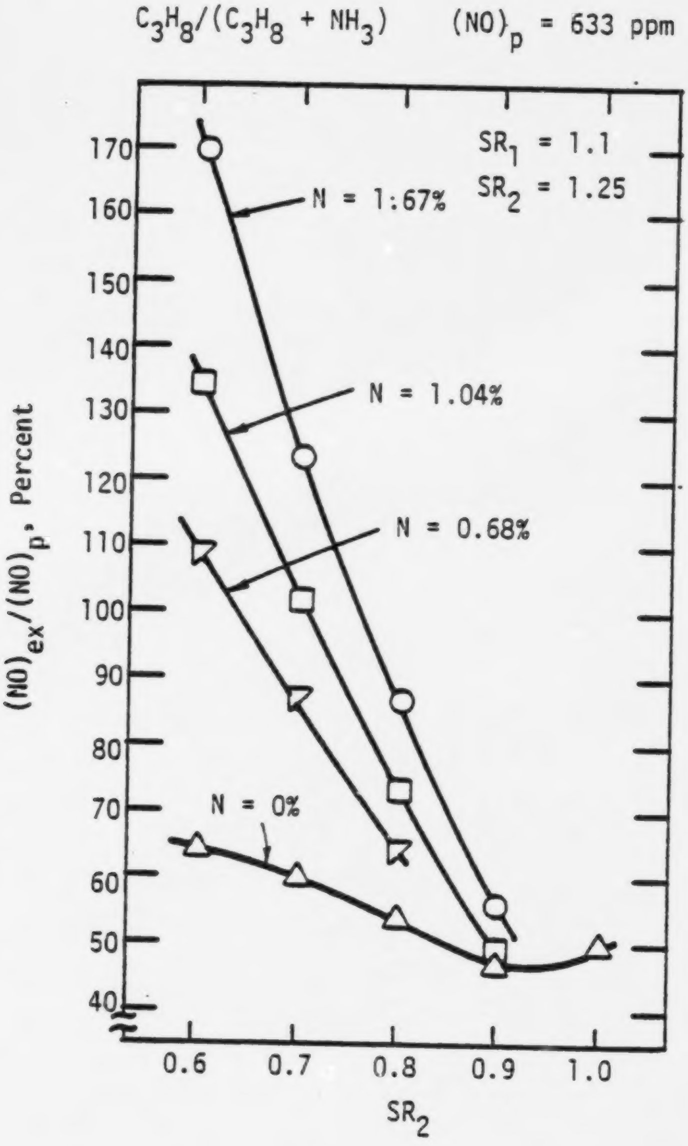


Figure 5-3. Effect of SR_2 and Reburning, Fuel Nitrogen Content, Tunnel Furnace -- Gaseous Fuels.

relatively little impact on reburning efficiency; however, at stoichiometries richer than 0.9, the nitrogen content of the reburning fuel is of critical importance. This could be particularly significant in a large practical system where there will be a large spectrum of local stoichiometries. It will clearly not be possible to instantaneously mix the reburning fuel across a 60-foot duct, and it is therefore unreasonable to assume that all local stoichiometries will be optimum.

5.2 Initial NO Concentration

Figure 5-4 shows results from Takahashi and coworkers on the influence of initial NO concentration on the decomposition in the secondary zone. These results indicate that under all fuel-rich stoichiometries studied the NO was almost totally decomposed irrespective of its initial level. These results suggest that the effectiveness of reburning should be relatively insensitive to initial NO level and Takahashi, et al. (1981), claim that 50 percent NO reductions can be achieved regardless of the NO level. This is particularly surprising because it is now well-established that N_2 formation is second order with respect to XN species concentration. Figure 5-5 shows the results of finite rate kinetic calculations conducted using the FCR/EER Kinetic Set to assess this effect. The reburning process was modeled with a 10 msec well-stirred reactor to simulate the fuel in the primary zone. The reactor effluent was mixed with the reburning methane over 25 msec and allowed to burn out for 300 msec. The initial NO level was varied to determine the influence of primary zone NO concentration and these results are shown in Figure 5-5. The calculations indicate that, as expected, the effectiveness of the reburning increases with increasing primary NO concentration. Figure 5-6 shows similar results obtained with the backfired reactor at the optimum secondary stoichiometry of 90 percent theoretical air. As predicted by the model, the fraction of NO removed by reburning with the nitrogen-free reburning fuel decreased with decreasing primary NO concentration. A similar but even sharper loss in effectiveness was observed when 0.5 weight percent NH_3 was added to the secondary fuel to simulate fuel nitrogen. In this case, the breakeven point where adding the reburning fuel containing 0.5 weight percent nitrogen neither increased nor decreased exhaust NO_x emissions, occurred at a primary NO concentration of approximately 160 ppm, corresponding to a primary conversion of about 3.5 percent. These results indicate that reburning becomes a more

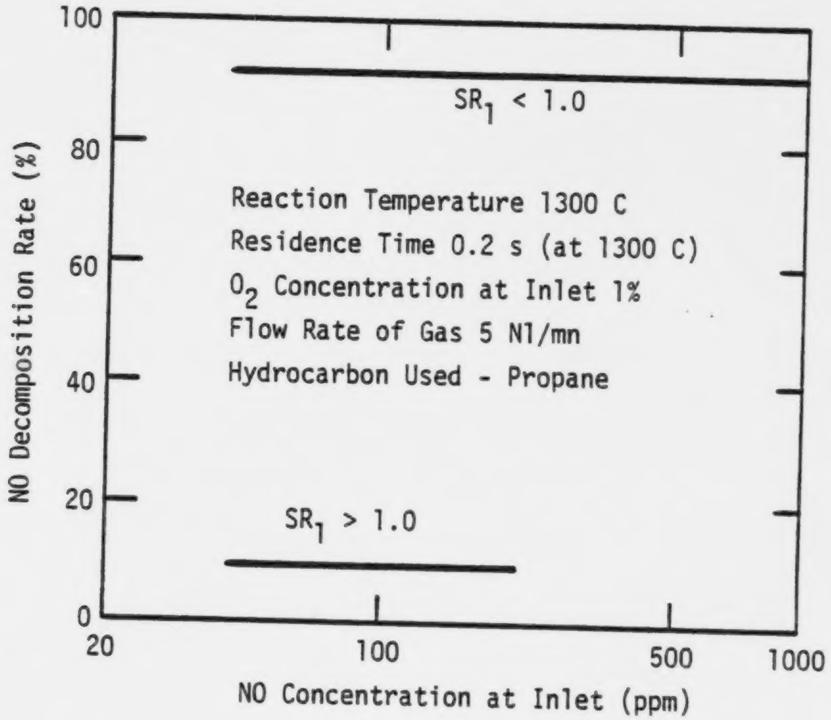


Figure 5-4. Influence of NO Concentration at Inlet on the NO Decomposition Rate.

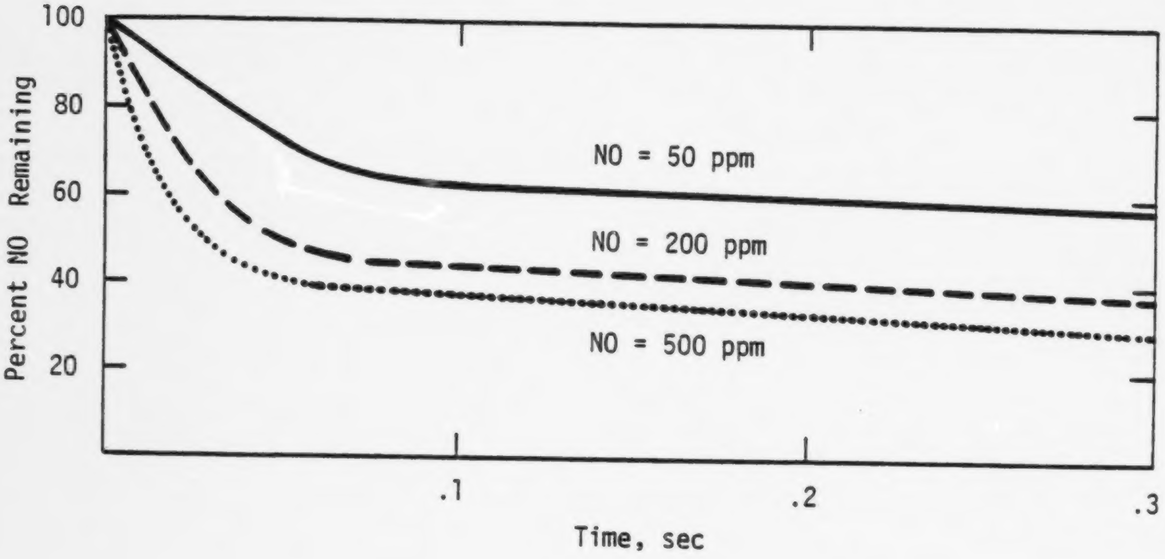


Figure 5-5. Effect of Initial NO Concentration and Time on Decay of NO (Kinetic Calculation Using FCR/EER Kinetic Set).

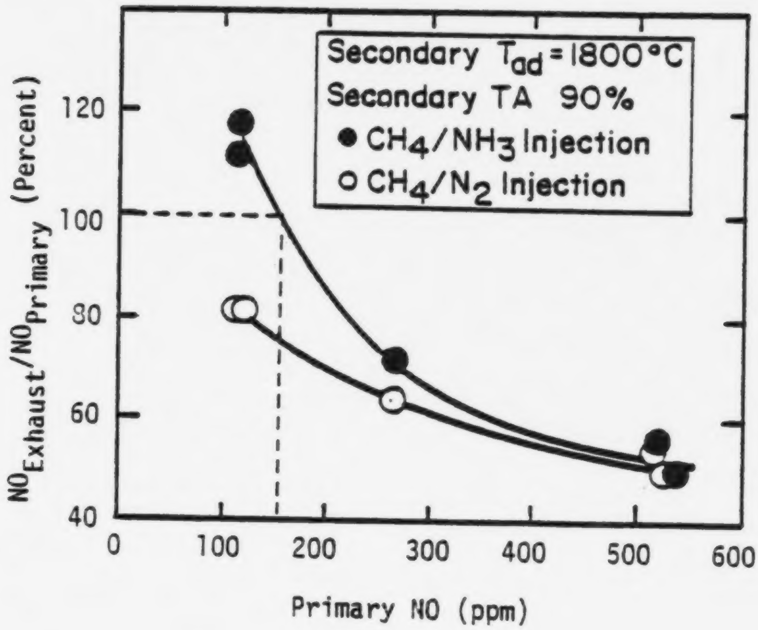


Figure 5-6. The Effect of Primary NO Level on the Effectiveness of Reburning With a Nitrogen-Free and a Nitrogen-Containing Reburning Fuel.

effective method for NO removal as the primary NO concentration increases; and, as noted before, the importance of reburning fuel nitrogen increases markedly as the primary NO decreases.

Figure 5-7 shows tunnel-furnace results where the reburning fuel nitrogen content was held constant at 1.04 weight percent N as NH_3 in propane and the primary zone NO concentration was varied from 148 ppm to 1118 ppm. These data again demonstrate the extreme importance of initial NO level on reburning efficiency, particularly at low-NO concentrations.

Similar tests were conducted in the tunnel furnace with the Beulah coal over a wide range of initial NO concentrations and secondary zone stoichiometries. Figure 5-8 summarizes these results; all of the data are shown in terms of the exhaust NO to primary zone NO ratio. As noted previously, as the secondary zone stoichiometry is reduced, the exhaust emissions generally decrease, go through a minimum at approximately SR_2 equals 0.9, and then increase due to the fuel nitrogen content of the reburning fuel. Figure 5-8 also indicates that, as with the bench-scale gas results, the effectiveness of the reburning concept depends heavily on the initial NO level. When the initial NO level was high (e.g., 2887 ppm), reductions as large as 75 percent were achieved with the reburning concept. However, when the NO level was relatively low (e.g., 148 ppm), reburning actually increased exhaust NO emissions at all stoichiometries.

Figure 5-9 summarizes the effectiveness of the reburning concept at the optimum second-stage stoichiometric ratio for the various primary NO concentrations. This figure emphasizes that it is clearly unreasonable to assume the application of reburning will always result in a 50 percent reduction in exhaust emissions. The effectiveness of the reburning process is clearly dependent on the initial NO level, the nitrogen content of the reburning fuel, and the overall combustion conditions.

Figure 5-10 summarizes all of the data taken with the propane/Beulah system for the different primary zone NO concentrations. In this case, the total NO in the exhaust (in moles per hour) is plotted against the molar flow rate of reactive nitrogen in the reburning zone (primary NO plus the nitrogen in the reburning coal). The solid symbols are the four different initial NO concentrations without any reburning fuel present. As expected,

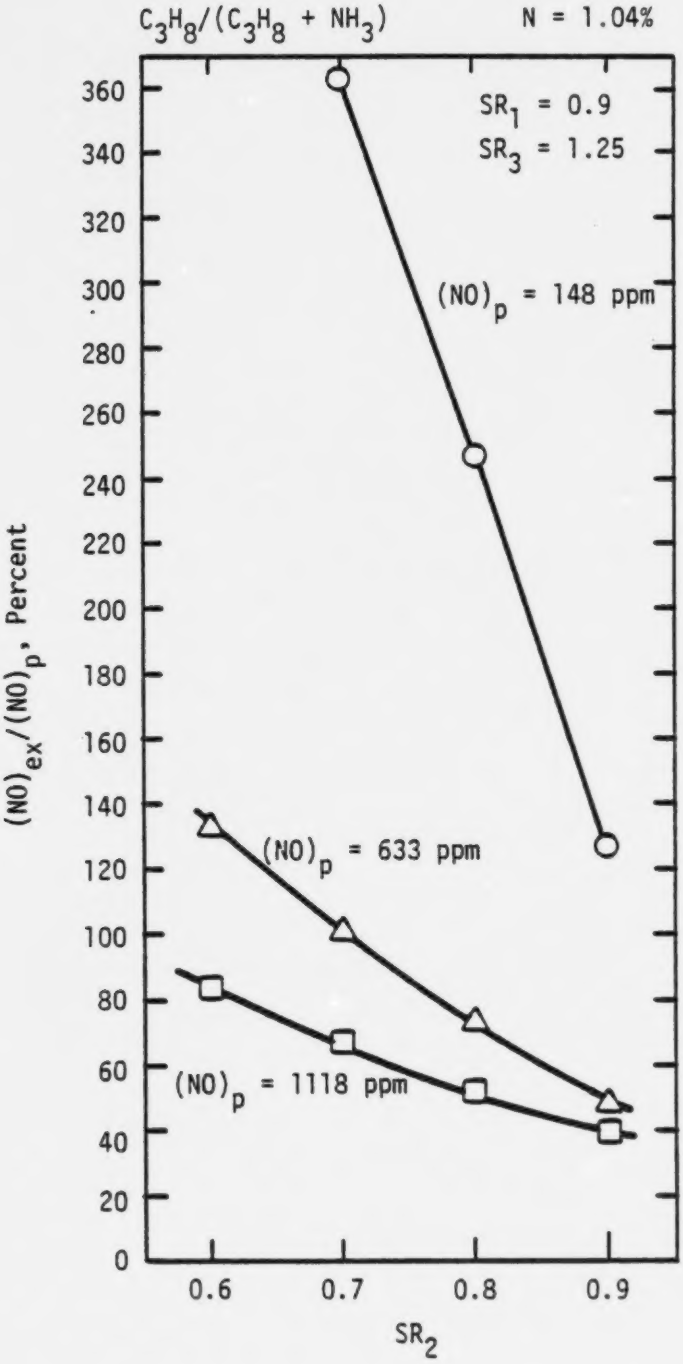


Figure 5-7. Effect of Primary NO (Tunnel Furnace).

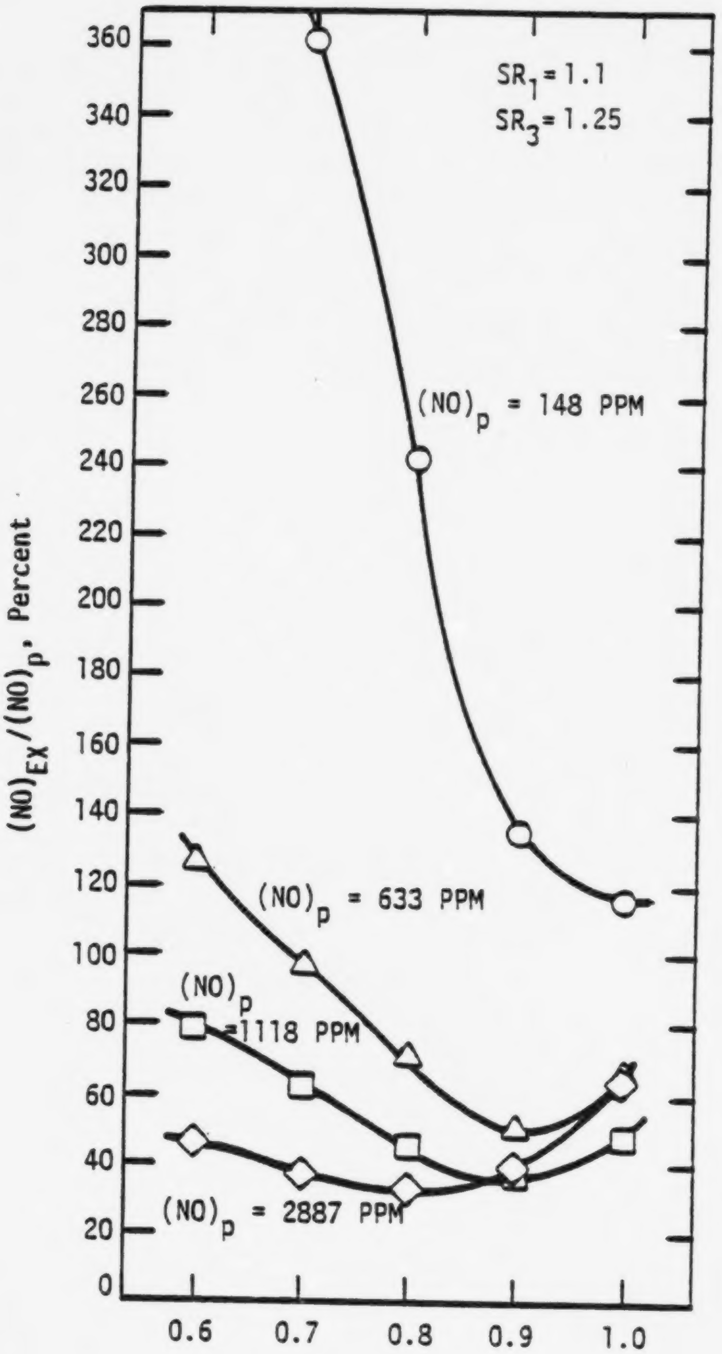


Figure 5-8. Influence of Primary Zone NO Concentration on Reburning Effectiveness from Tunnel Furnace (Propane/NH_3 - Beulah Lignite).

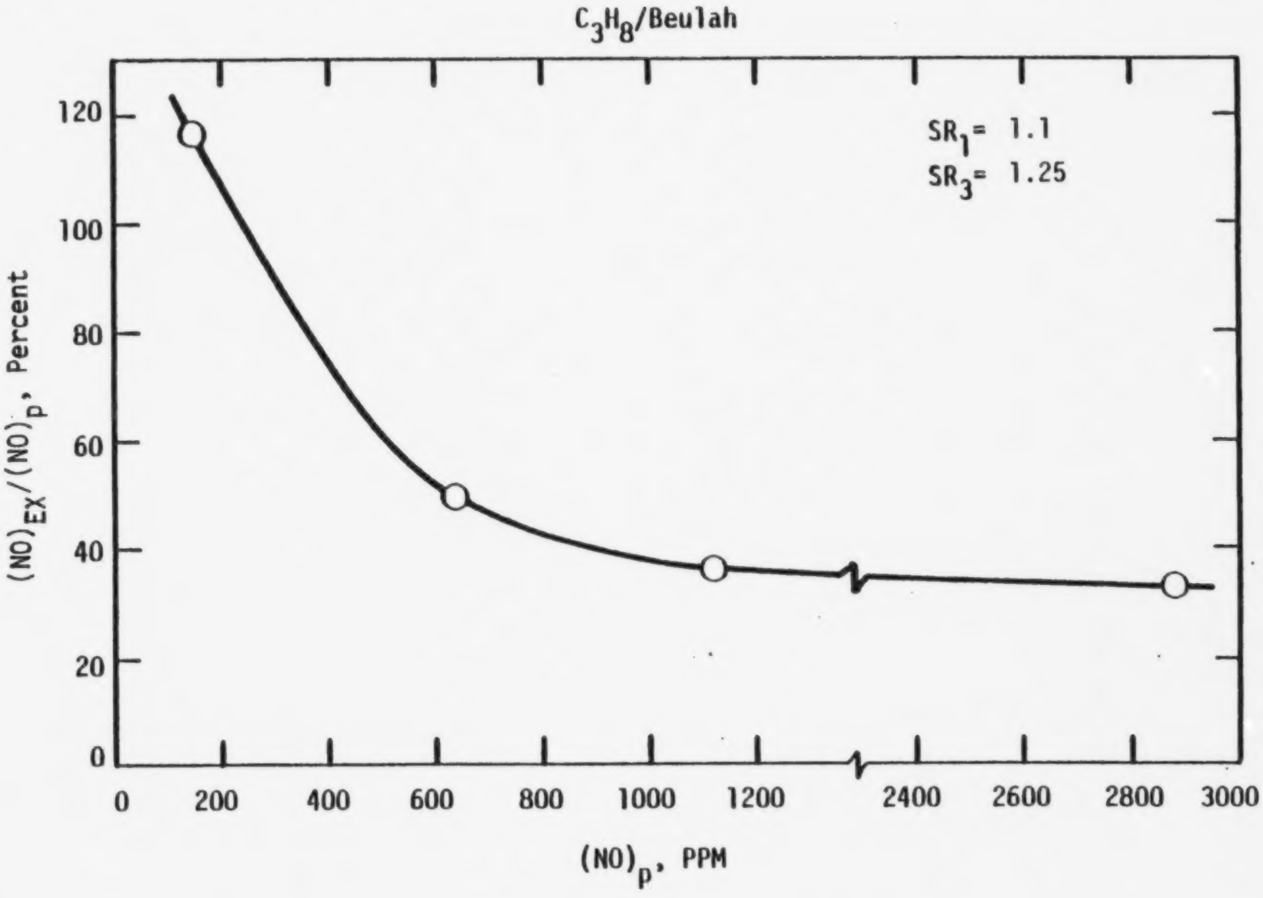


Figure 5-9. Effect of Primary Zone NO Concentration at Optimum SR_2.

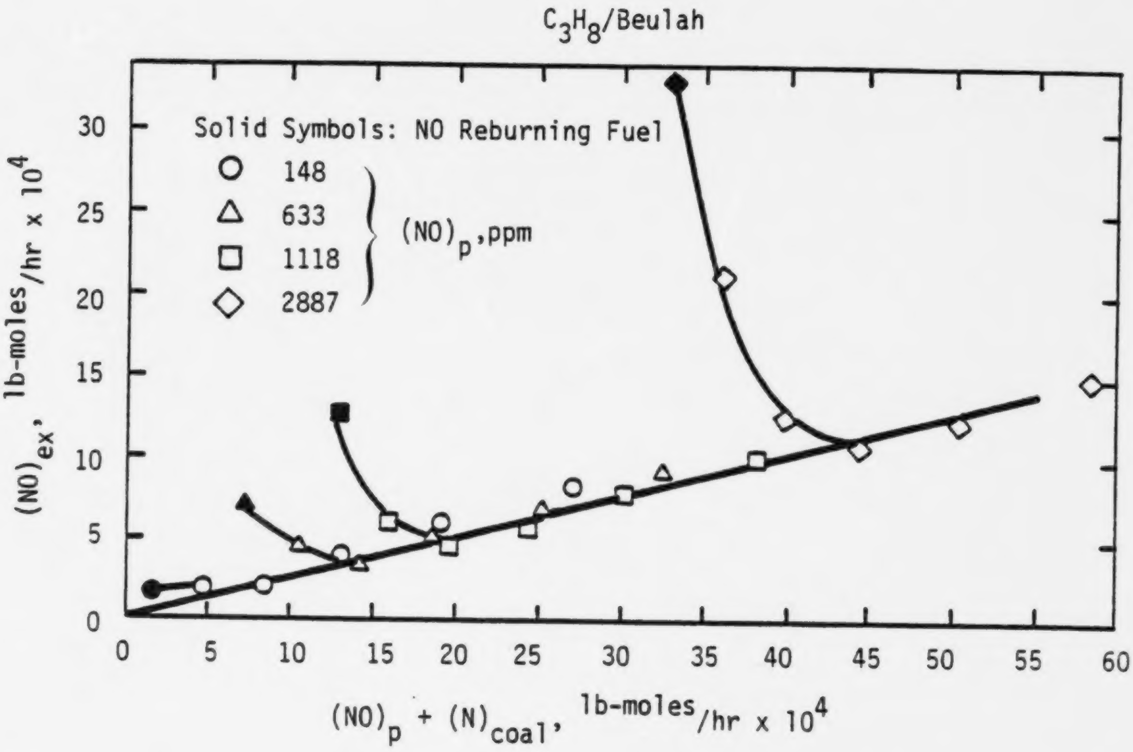


Figure 5-10. Importance of Total Available Nitrogen (Primary NO Plus Fuel Nitrogen).

the exhaust emissions increased essentially linearly with increasing primary NO when no reburning fuel was present. In general, as the reburning fuel is increased, the NO emissions decrease until they reach an effective "operating line." As further reburning fuel is added (due to decreases in SR_2), the origin of the nitrogen becomes less important; increasing the reactive nitrogen content of the fuel-rich reburning stage, either by increasing the primary zone NO or by adding additional fuel, results in increased NO emissions. Clearly the slope of the line is a strong function of the coal composition, the combustion conditions, and the stoichiometry distribution throughout the furnace. However, its existence demonstrates the importance of both fuel nitrogen content of the reburning fuel and initial NO level in general. Further, if the primary zone NO concentration is low and below the overall operating line, then the addition of any reburning fuel will increase the exhaust NO emissions (circles).

5.3 Coal Composition Effects

To explicitly investigate the influence of reburning fuel composition on the achievable NO_x reduction, several tests were conducted. In each case, the primary zone was fired with propane and doped with NO to provide constant temperature and concentration profiles at the inlet of the reburning zone. Figure 5-11 shows the influence of the rich-zone stoichiometry (SR_2) as a function of the reburning fuel. These tests were conducted with propane plus ammonia, and Beulah coal as the reburning fuels. These results again indicate that under optimum stoichiometry conditions ($SR_2 = 0.9$) for high initial NO concentrations the composition of the reburning fuel has relatively little influence on the effectiveness of the reburning process (particularly the NO reduction step). Figure 5-12 compares the Beulah coal data with the propane plus ammonia data (both as the reburning fuel) with matched nitrogen contents as a function of the primary zone NO concentration. These results show that at the optimum stoichiometry condition the propane-ammonia simulates the Beulah coal performance quite well. The data strongly suggest that heterogeneous effects are of second-order importance.

Figure 5-13 shows the results from tunnel furnace tests where a variety of coals were used as the reburning fuel. Throughout these tests the rich-zone stoichiometry was 0.9 (optimum) and the furnace was uncooled. These

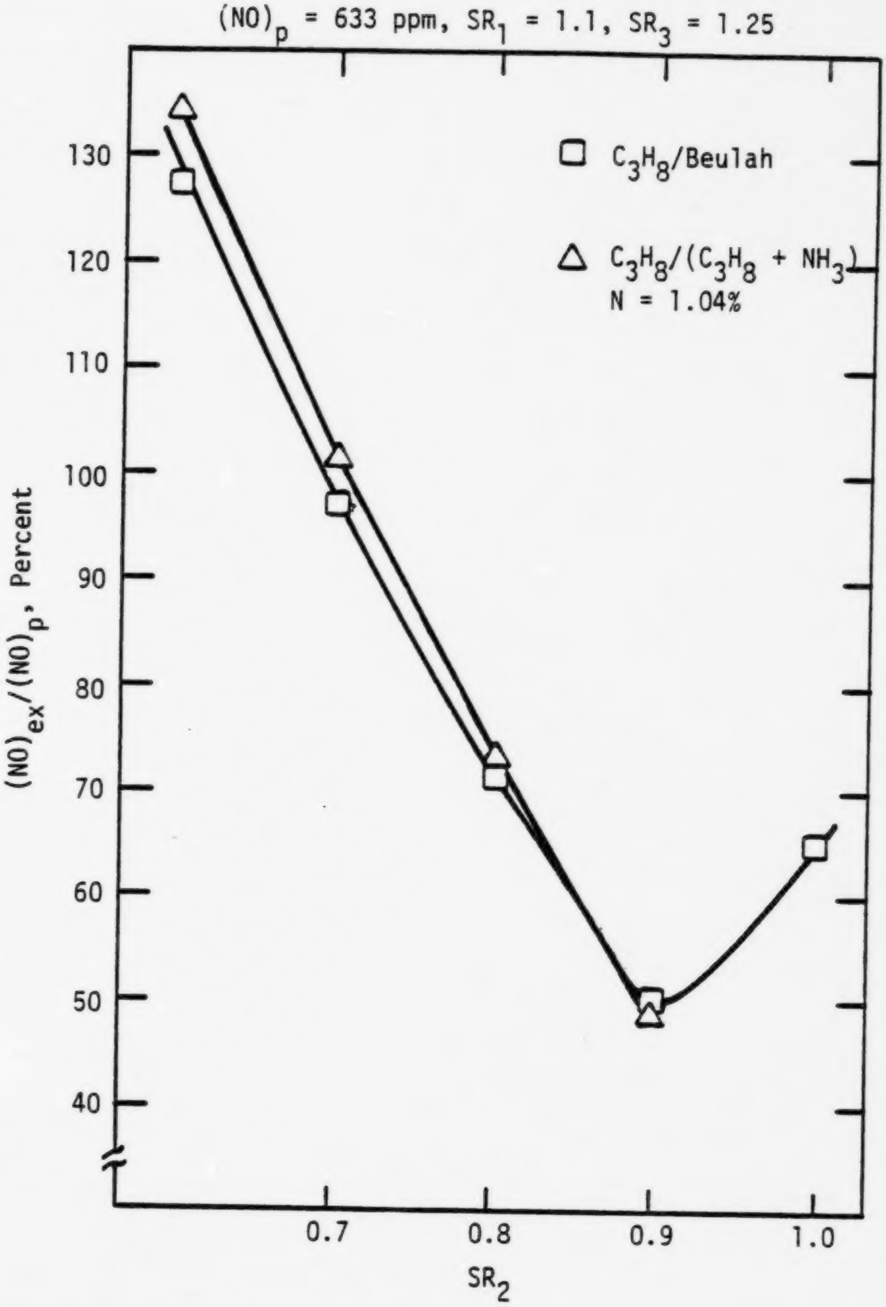


Figure 5-11. Comparison of Coal and Propane - Influence of SR_2 (Tunnel Furnace).

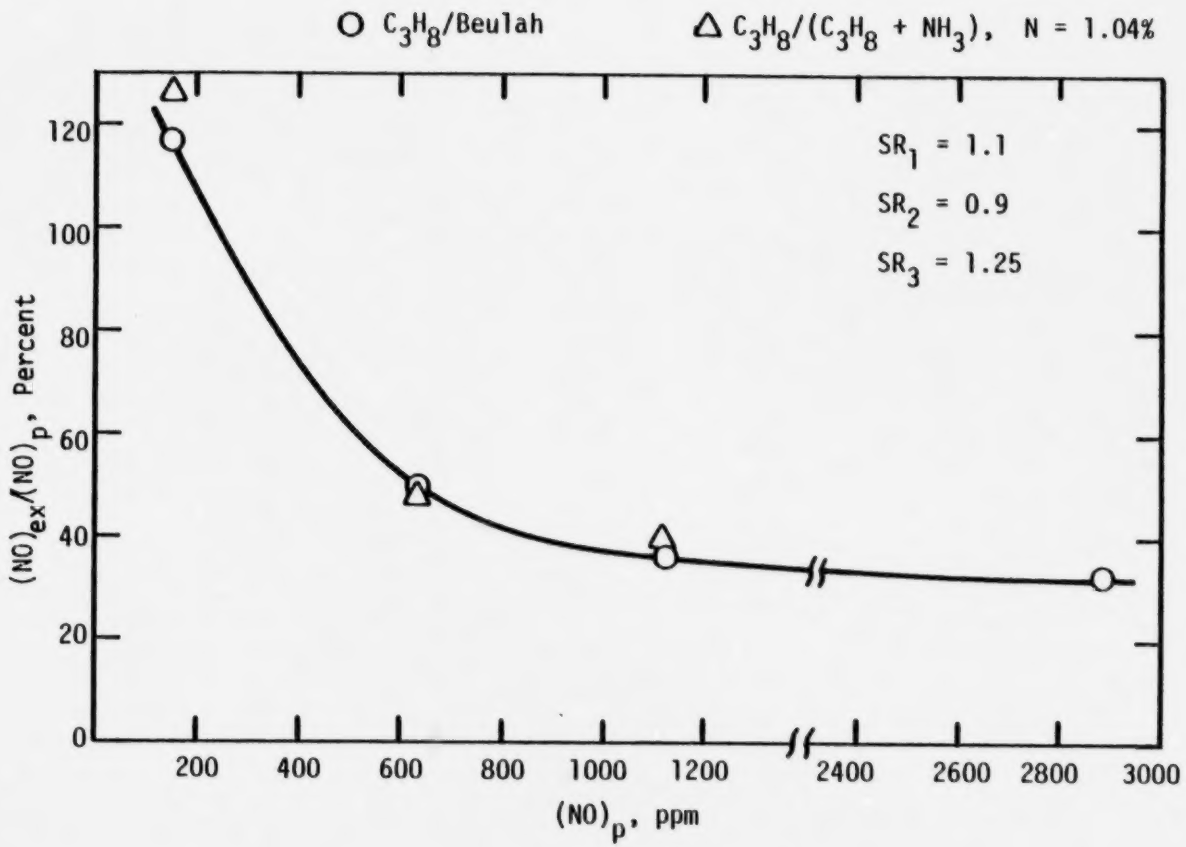


Figure 5-12. Influence of Reburning Fuel Type and Primary NO Level (Tunnel Furnace).

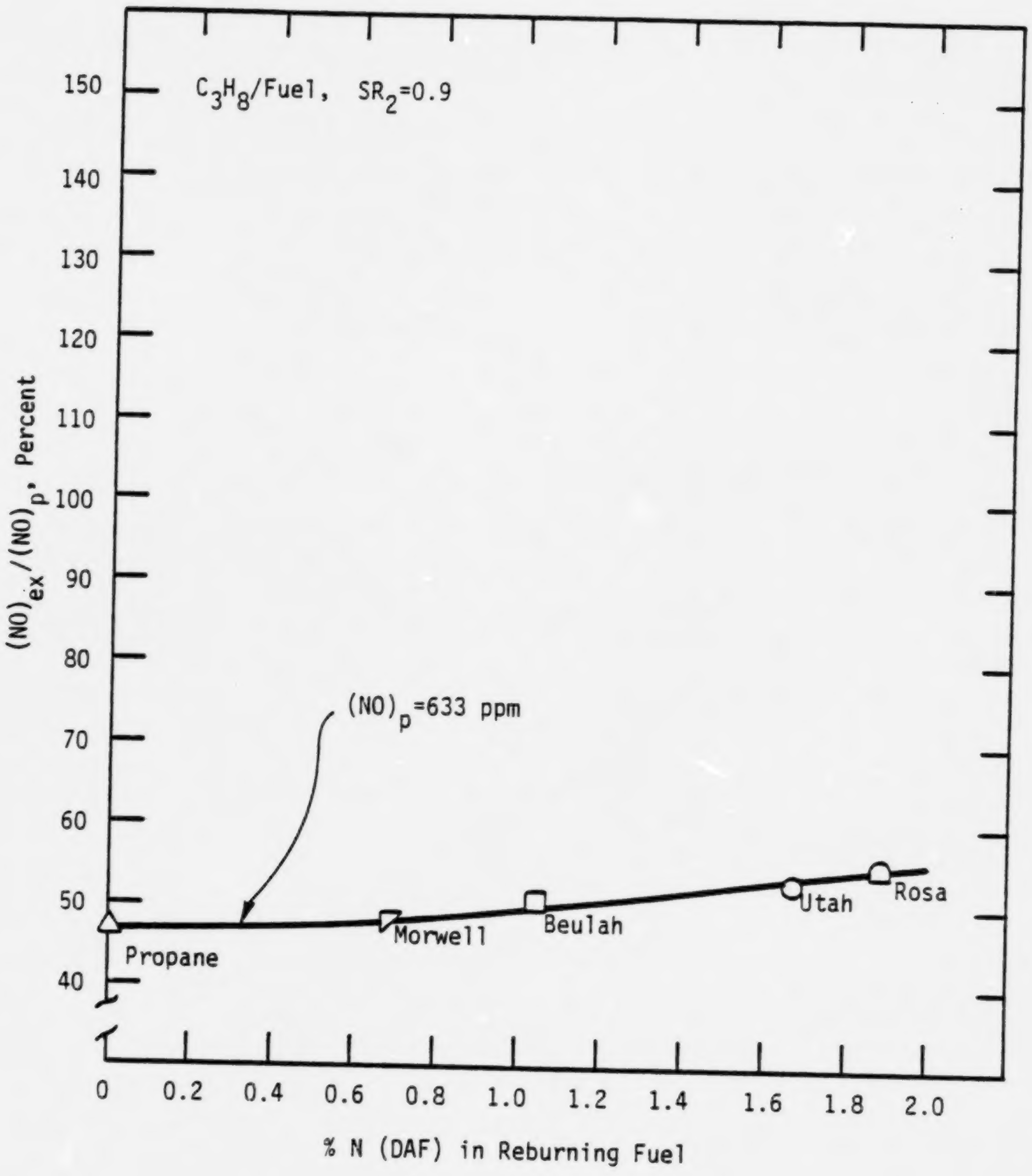


Figure 5-13. Impact of Nitrogen in Reburning Fuel on NO_x Reduction.

data indicate that as the nitrogen content of the reburning fuel increased, the effectiveness of the reburning only decreased slightly when the initial NO level was high; however, when the primary NO level was reduced to 148 ppm, the nitrogen content of the reburning fuel became more important. In addition, the Rosa coal results indicate that reburning with real American coals can be far more complex than suggested by Takahashi and coworkers because with this medium-volatile bituminous coal almost 10 percent of the reburning fuel was unburned (emitted as carbon particulate) even at the optimum reburning conditions.

Figure 5-14 summarizes all of the results obtained with the different reburning fuels. In all cases, the primary fuel was propane-doped to produce 633 ppm NO in the primary exhaust. These data indicate that coal composition has a relatively strong influence on the general reburning performance of the solid fuel. Even though the Utah coal contains a relatively large amount of fuel nitrogen, its overall performance was superior to that of the other fuels. This is believed to be because the Utah coal has a high-volatile nitrogen fraction and produces large amounts of hydrocarbons in contrast to the medium-volatile Rosa and the low-rank Beulah and Morwell coals. These results strongly suggest that it is erroneous to assume that all coals will behave equally well with respect to reburning effectiveness at other than optimum conditions.

Figure 5-15 compares the results obtained with Utah and Beulah coals fired in both the primary and reburning stages. In this figure, the data are plotted on an emission factor basis and they effectively summarize the complications associated with real fuels. The Utah coal contains approximately 60 percent more fuel nitrogen than the Beulah coal and the uncontrolled NO emissions for the Utah coal are approximately 60 percent higher (1028 ppm vs. 625 ppm). However, under the optimum reburning conditions (SR_2 = 0.8) the emissions from the Utah coal were only about 30 percent higher than those from the Beulah lignite. This is due to both the difference in primary NO level (Utah contains more volatile, reactive fuel nitrogen) and the difference in the reburning effectiveness. Reburning was less effective overall with the Beulah coal because the initial NO was lower, the combustion zone temperatures were lower (Beulah has a high moisture content), the nitrogen in the Beulah lignite tends to remain in the solid phase, and the Beulah

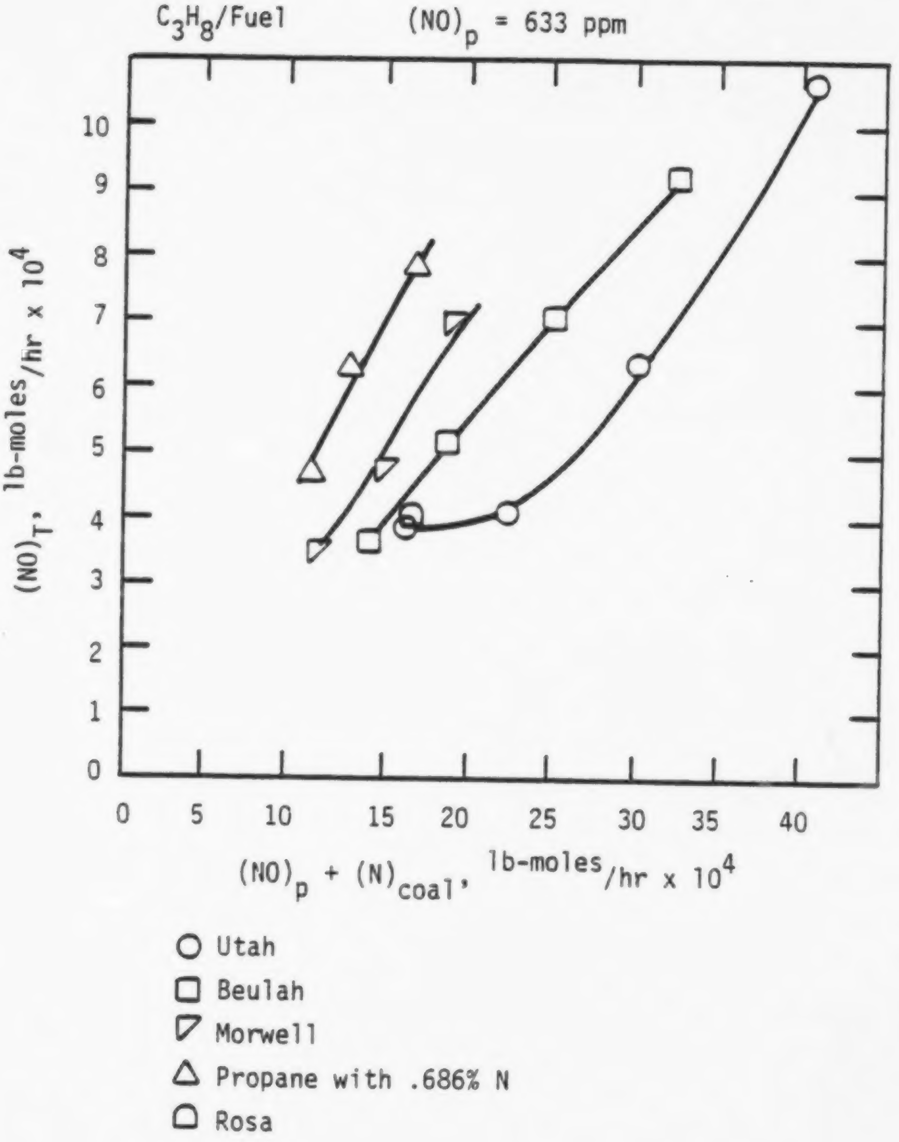


Figure 5-14. Importance of Coal Composition in Reburning.

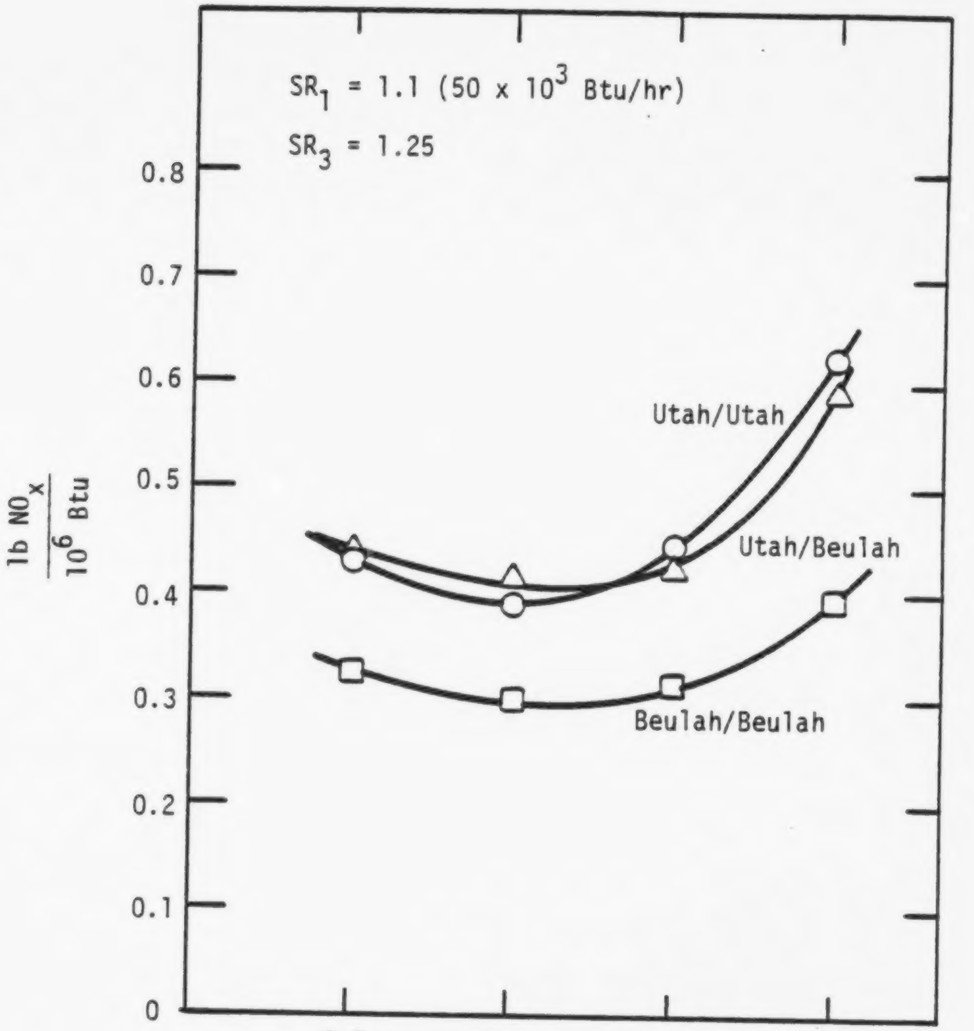


Figure 5-15. Overall Effect of Fuel Composition in Tunnel Furnace.

coal tends to produce more CO (less CH) species than the Utah coal. Thus, in a practical system, the exhaust NO_x emissions will depend strongly upon the coal combustion characteristics, even when reburning is applied.

6.0 INFLUENCE OF THERMAL ENVIRONMENT

The purpose of this section is to discuss the influence of the thermal environment on both the NO reduction in the second stage and the XN oxidation in the final stage of the reburning process. This effect has been separated from the other combustion parameters because of the complexities associated with thermal history and the thermal coupling which can occur between stages. This section begins by reviewing the information currently available from other staged combustion studies. Gas-phase reburning results are then considered, and the section concludes with actual coal reburning data.

6.1 Background Results

It is now well-established that thermal history can have a significant influence on the fate of nitrogen species under fuel-rich and staged combustion conditions. England, et al. (1981), have shown that in liquid-fuel-fired systems, it is desirable to have a nearly adiabatic first stage to promote the evolution of the nitrogen from the liquid phase and maximize the rate of the XN species decay toward their low equilibrium levels prior to the addition of the second stage air. However, Johnson, et al. (1979), found that with pulverized coal, significant heat removal was beneficial with respect to overall NO_x emissions. Chen, et al. (1982) found similar results for pulverized coal and defined the overall mechanisms by investigating the component processes. These results indicate that decreasing the primary-zone temperature tends to increase exhaust NO_x because it decreases the rate of TFN decay in the rich zone and increases the amount of char nitrogen carried into the excess air region. However, in general, these effects are more than compensated by a marked decrease in the conversion of gas-phase TFN species in the final excess air flame. In particular, these investigators have postulated that increased heat extraction reduces exhaust NO_x emissions because of selective reduction of NO by NH_i species in the final zone. The composition and thermal conditions required for this effect to occur are similar to those defined by Lyon (1975) for external "de-NO_x."

Chen and coworkers have further shown that the effectiveness of increased heat extraction depends heavily on the composition of the coal being burned. With low-rank coals, increasing the heat removal only reduced exhaust NO_x emissions at high stoichiometries (SR_1 greater than 0.7). Increased cooling had little effect on the TFN concentrations; however, at very rich conditions, it increased the carry-over of solid nitrogen. Thus, in these cases the decreased emissions associated with reduced gas-phase conversions were mitigated by increased contributions from char nitrogen. Alternatively, with some high-volatile bituminous coals, reducing first-stage temperature actually had no effect on the overall exhaust NO emissions. Detailed internal measurements indicated that this was because the decreased TFN conversion was completely compensated by significant increases in the first-stage NO emissions. This effect was particularly prominent with high-rank bituminous coals which produced little NH_3.

6.2 Gas-Phase Chemistry

Figure 6-1 shows the data of Takahashi and coworkers on the influence of local temperature on the homogeneous decomposition of NO in the rich zone. These results indicate that at stoichiometries greater than 1.0 the decomposition is low and essentially independent of temperature. However, at SR_2 levels below 1.0, the NO decomposition proceeds rapidly (residence time 0.2 seconds) and essentially is complete for temperatures above 1200°C. These results are very similar to previous work by Muzio, et al. (1976) wherein ethane was injected into NO-laden streams. Figure 6-2 shows results for the second half of the reburning process (XN oxidation). In this case, it is clearly desirable to operate at conditions between approximately 700 and 900°C because less of the XN intermediates are converted to NO in the excess air flame. This coincides almost exactly with the 800 to 1000°C local flame temperature recommended by Lyon (1975) for selective NH_i plus NO reactions.

Figure 6-3 shows the results of finite kinetic rate calculations for the fuel-rich stage of the reburning process. These results indicate that stoichiometries below approximately 0.9 and temperatures above approximately 1300°C are theoretically required for rapid NO destruction in the fuel-rich zone.

Figure 6-4 shows experimental data on the influence of overall temperature with gaseous fuels. These results were obtained with the backfired bench-scale reactor using methane as the reburning fuel. The data shown in Figure 6-4 indicate that increasing the temperature significantly increases the amount of NO reduction in the rich zone (due to an increased rate of N_2 formation). Increased temperature also increases the conversion of the XN

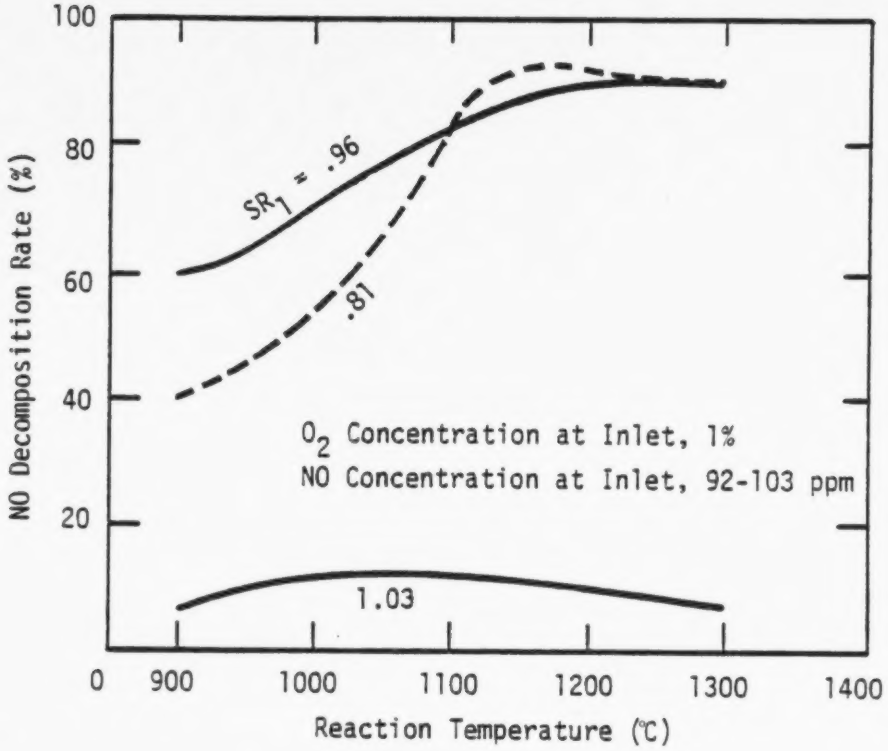


Figure 6-1. Influence of Reaction Temperature on the NO Decomposition Rate (after Takahashi, 1981).

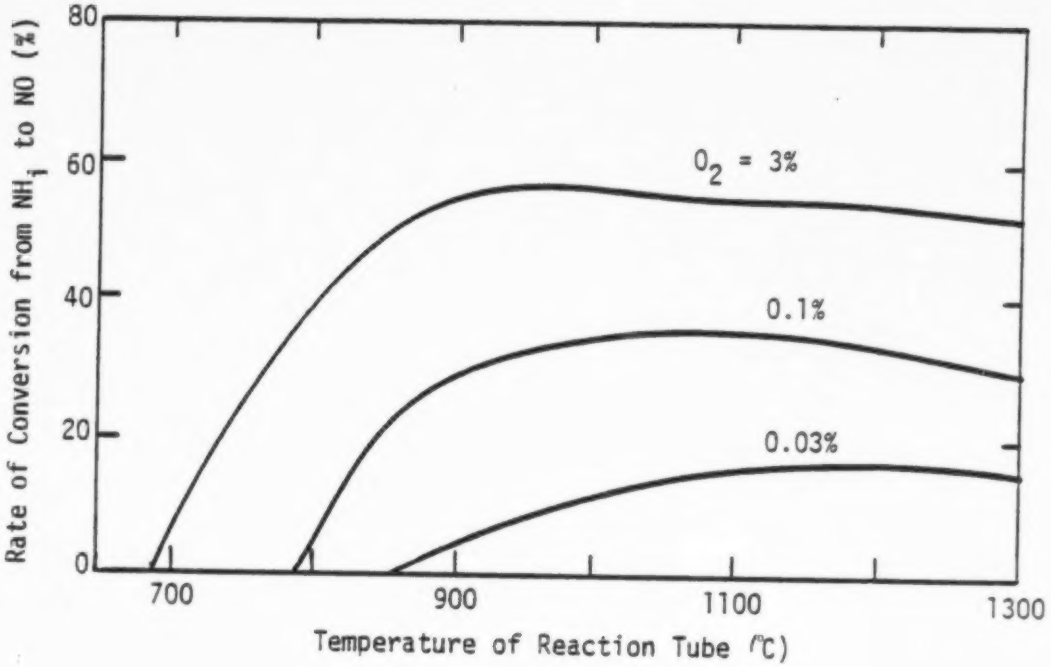


Figure 6-2. Conversion Rate from NH_i to NO in XN Oxidation Process. From Takahashi, et al., 1981.

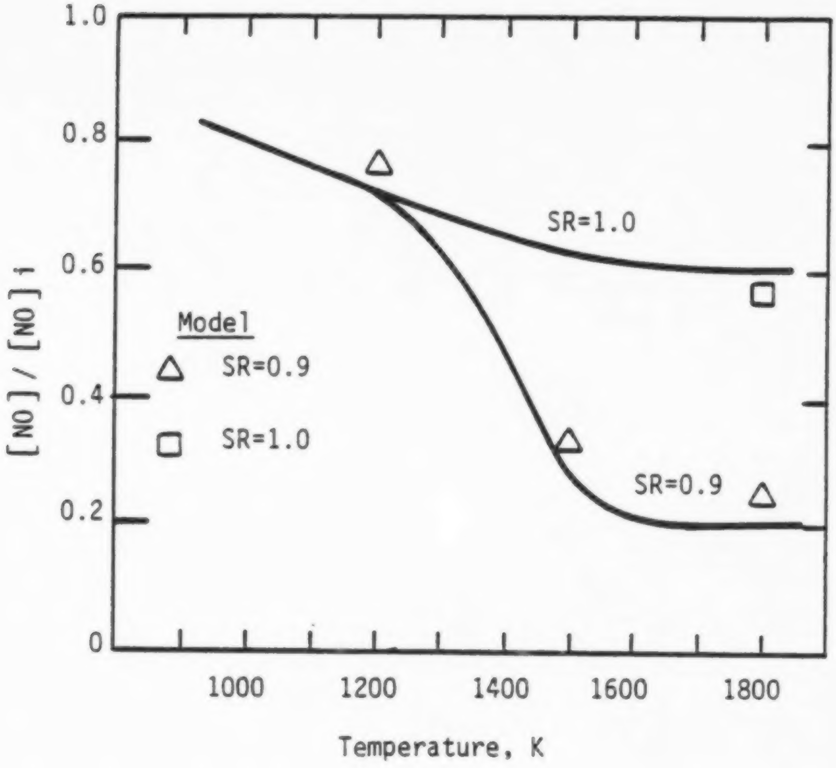


Figure 6-3. Comparison of Analytical and Experimental Influence of Reduction Zone Temperature on NO Reduction (Experimental Data After Muzio, 1976, Shown with Solid Lines; Predictions Using FCR Kinetic Set).

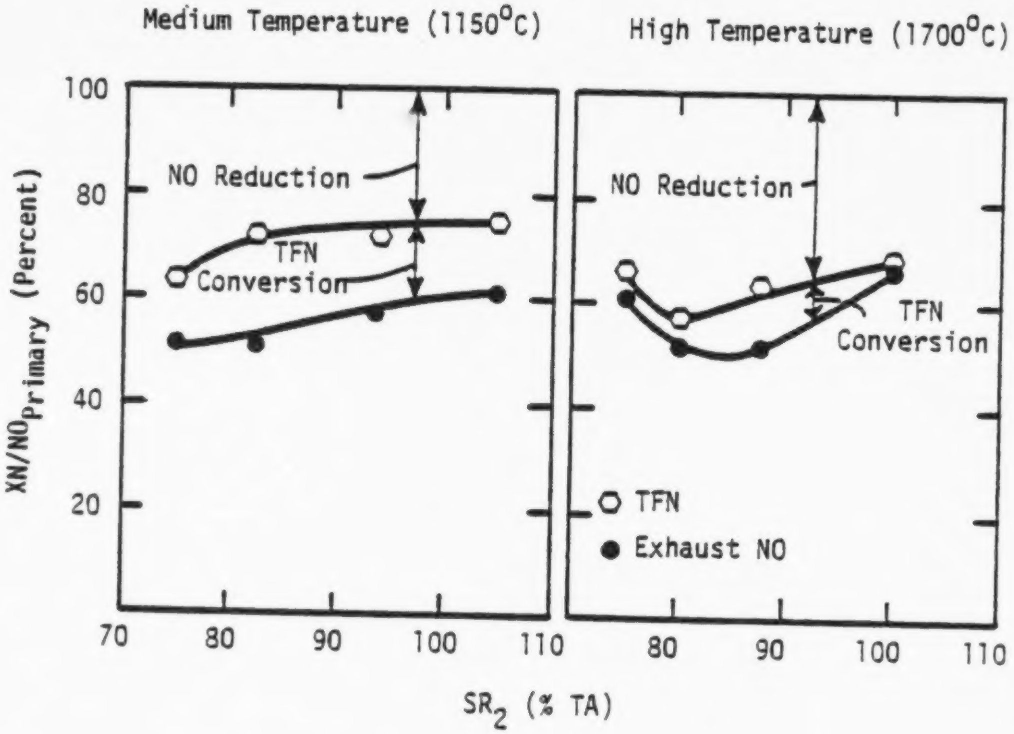


Figure 6-4. NO Reduction and TFN Conversion at Two Temperatures (CH_4/N_2 as the Reburning Fuel).

species to NO and, hence, decreases the effectiveness of this process for NO control.

6.3 Coal Results

A series of coal studies was conducted in the tunnel furnace to investigate the role of thermal environment on the effectiveness of the reburning concept. In these experiments, cooling coils were placed in the secondary (fuel-rich) stage. Figure 6-5 summarizes the overall results of these studies where propane was the primary-zone fuel and the Beulah North Dakota lignite was the reburning fuel. Throughout the testing, the primary zone stoichiometry was held constant at 1.1 and the overall stoichiometry was 1.25. Figure 6-5 illustrates that the addition of secondary cooling dramatically reduced the exhaust NO emissions for both primary-zone NO concentrations (633 and 148 ppm). In an effort to understand the mechanism of this effect, detailed XN species measurements were made at the outlet of the secondary (fuel-rich) zone and these results are summarized in Figure 6-6. Cooling had relatively little effect on the concentrations of HCN and NH_3 leaving the rich zone (except at the extremely low secondary stoichiometries); however, decreasing the temperature of the rich zone significantly decreased the rate of NO decay within the rich zone and resulted in a much larger char nitrogen carry-through. These results are essentially identical to those measured previously by Chen, et al. (1982), for normal staged combustion systems. Decreasing the temperature of the rich zone tends to retard both the formation of N_2 from the gas-phase TFN species and the evolution of nitrogen from the solid phase. Figure 6-7 shows the overall TXN (including char nitrogen) for both the normal and cooled case. The significant increase in TXN with cooling is the direct result of the higher NO and char nitrogen concentrations. Figure 6-7 also shows the overall conversion of the TXN to exhaust NO and indicates that the reason decreasing rich-zone temperature results in reduced exhaust emissions (Figure 6-5) is that the conversion of the reactive nitrogen which enters the tertiary stage, greatly decreases in the cooled case. (Admittedly, the overall conversion phase shown in Figure 6-7 is an integrated average of the gas-phase and solid-phase conversion, but there can be little doubt of the overall effect of cooling.) The dramatic decrease in the TXN conversion at reduced temperatures is believed to be the result of selective NO reduction by NH_i species as proposed

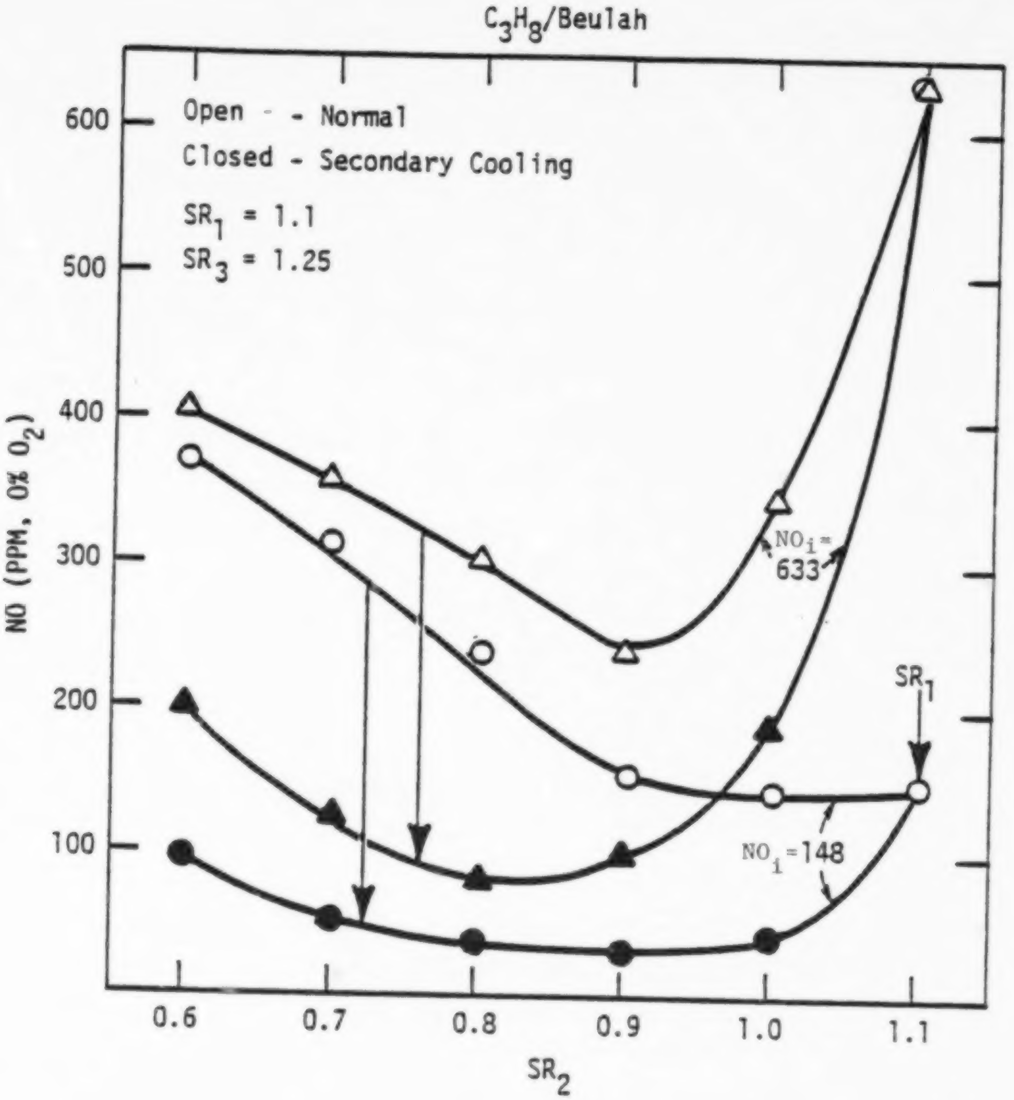


Figure 6-5. Effect of Secondary Cooling on Exhaust NO Emissions.

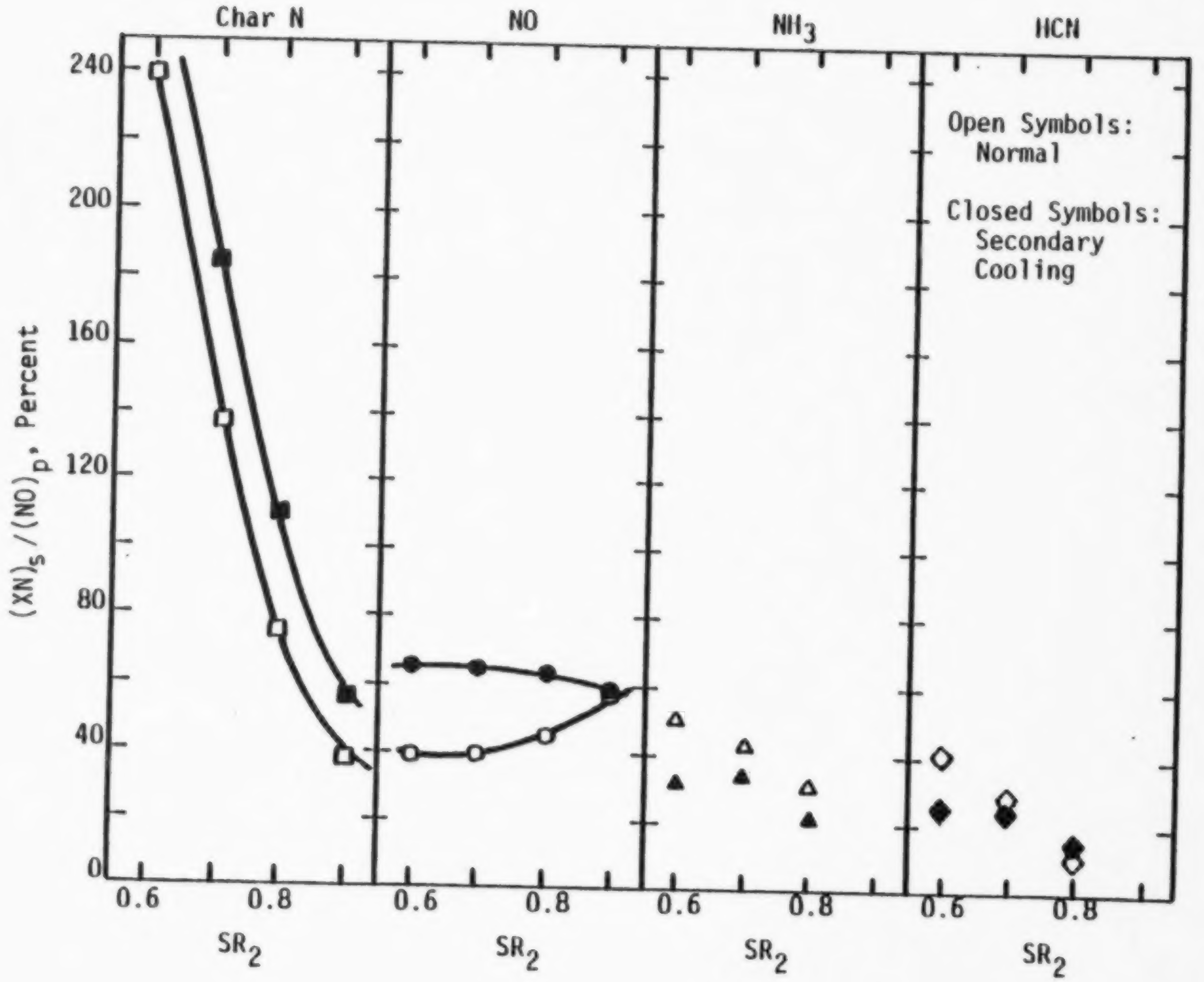


Figure 6-6. Effect of Secondary Cooling on Species Concentrations at the Second Stage Exit.

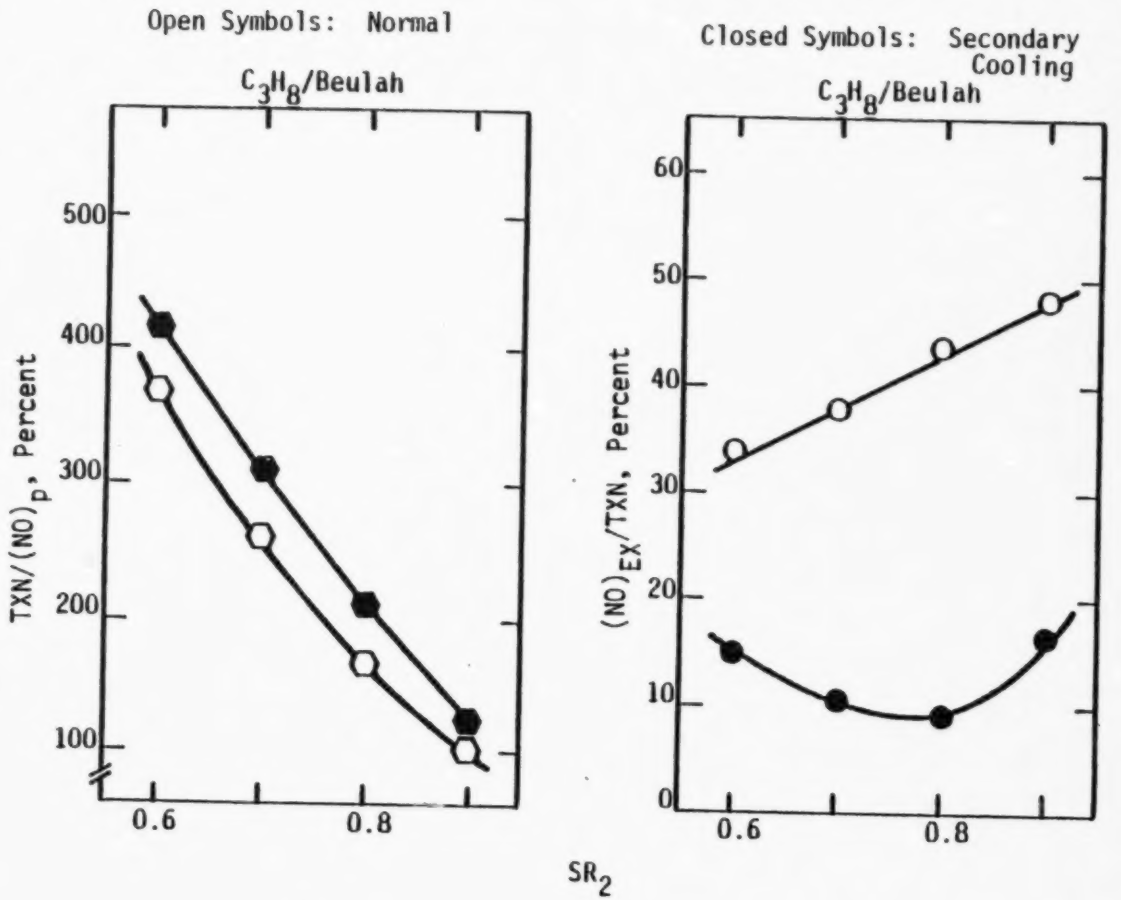


Figure 6-7, Secondary Cooling: Effect on TXN Formation and Conversion.

by Lyon (1975). Figure 6-8 shows the gas-phase temperature measured at the exit of each zone and indicates that in the cooled case the reactants entered the third zone (XN oxidation) at approximately 800 C. Thus, in this case the local flame temperatures in the oxidation zone were in the ideal region (800 - 1000 C) for selective NH_i reduction.

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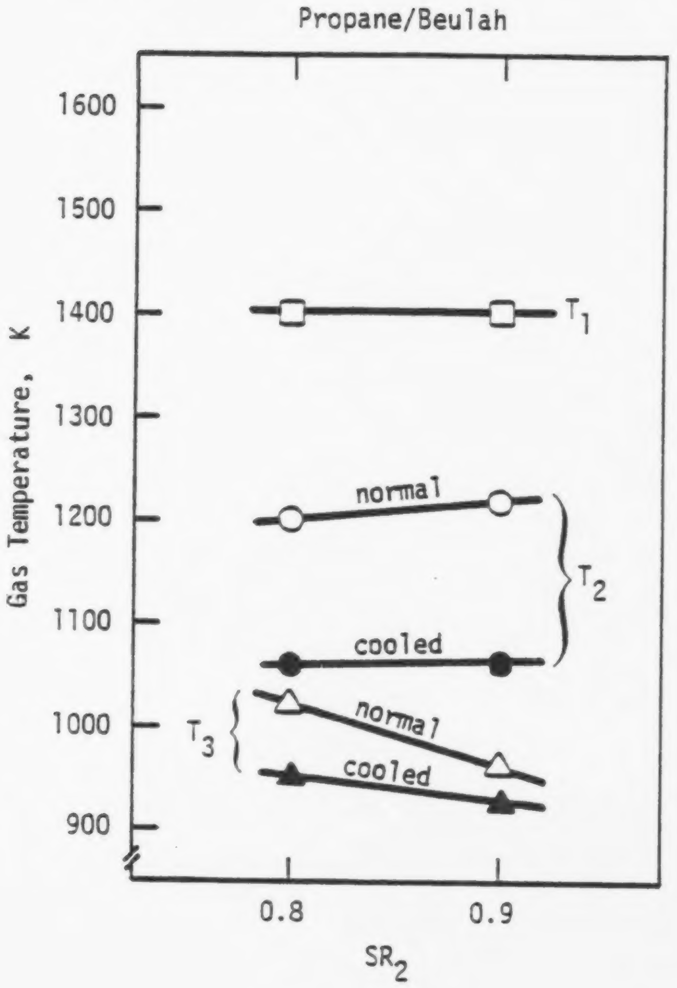

Figure 6-8. Detailed Temperature Measurements.

APPENDIX A

GAS PHASE REACTIONS OF IN-FURNACE NO_X REDUCTION

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1.0 INTRODUCTION

The potential for the reduction of NO_x by multiple stage processing has been known for almost a decade. In all applications of staged combustion concepts for NO_x control, the equilibrium level of NO is much lower than the actual levels attained. This is due primarily to the relatively slow kinetics associated with fuel nitrogen processing. Many of the concepts are designed to yield conditions that will enhance the kinetics, e.g., high temperatures, long residence times, and rich conditions. The reburning or in-furnace NO_x reduction approach attempts to get around the kinetic limitations by multiple staging the combustion process so that the fast reactions which occur in the flame zone can be utilized more effectively. The envisioned application of the reburning approach is to inject a small portion of fuel after the typical rich/lean staged burner zone. After this reduction zone, air is added to burn out the reburn fuel.

A short, fast response task was undertaken in the Fundamental Combustion Research program to investigate the key gas phase reactions and limitations of the reburn process. This task combined an analytical modeling subtask as well as a lab-scale experimental subtask to address the influence of key process parameters: temperature, stoichiometry, initial NO level, mixing levels and residence times. The overall objective was to indicate the requirements of the system which makes use of the reburn concept and to indicate future research needs.

The first description of the reburn concept is contained in the work of Wendt et al. (1973). In this work methane was added to the post-flame gases of an NO-seeded CH_4/air flat flame (110 percent theoretical air, 1.75 percent C_2 in exhaust, 1100 ppm NO). The reburn CH_4 provided overall equivalence ratios of 0.91 to 1.27. Reduction of about 50 percent of the NO was noted. However, the fuel-rich stream was not burned out by the addition of O_2, and reduced nitrogen species (NH_3 and HCN) were not measured. Thus, the actual reduction of fixed nitrogen into N_2 cannot be determined.

Recent Japanese work (Takahashi et al., 1981) has led to MACT (Mitsubishi Advanced Combustion Technology) in-furnace NO_x removal technology. This reburn technology has been demonstrated in laboratory-scale studies, in a pilot plant, and in a reduced-scale industrial burner.

The laboratory-scale experiment consisted of two electrically heated porcelain flow tubes connected by a constricted quartz joint. Fuel-rich mixtures of fuel, oxidizer, nitrogen and NO were mixed and passed into the first tube. At the end of the first tube, O_2 was added to complete burnout. The constricted quartz joint provided mixing for the second tube. The results indicated:

- An insensitivity to residence times longer than 0.1-second.
- An increasing conversion rate with temperature to up to ca. 1200°C.
- Virtual independence of the reaction to initial NO concentration for $50 < NO < 1000$ ppm.
- The reaction occurs most favorably with a secondary stoichiometry that corresponds to 1.25 to 2.5 times the fuel needed to burn out the O_2 leaving the primary.

Pilot-scale data were obtained from a 100 kg fuel/hour test facility. Pulverized coal or propane were burned with sufficient excess air to yield one percent O_2 in the flue gas. An amount of fuel equal to about 10 percent of the inlet fuel flow was injected into the primary stream by a secondary burner. Tertiary air addition makes the combustor overall fuel-lean and oxidizes all fixed nitrogen into NO. No NH_3 or HCN was noted in the fuel-lean section. A 50 percent reduction of primary NO was achieved. Wendt et al (1979) also noted a reduction in pilot-scale pulverized coal NO_x emissions upon reburning with CH_4.

The reduced-scale industrial burner tests were performed in a 1/5th-scale tangentially fired furnace. Test fuels included propane, heavy fuel oil doped with pyridene and a domestic Japanese coal. Again, a repeatable 50 percent reduction of NO was obtained. Especially significant is the fact that this reduction appears to be independent of inlet NO (i.e., propane firing, with 20 ppm inlet NO showed the same fractional reduction as the coal, with 200 ppm inlet NO). As with the previous tests, no tertiary NH_3 or HCN were observed.

In an earlier study Myerson (1975) studied the hydrocarbon-NO reaction in a heated flow tube. The hydrocarbons, NO and oxygen were heavily diluted in products typical of post flame gases. Experimental results included:

- Increased temperature favored removal.
- At low temperatures (1256 K) NO showed a sharp minimum with stoichiometry. At higher temperatures this turned into a transition between low reduction (fuel-lear) and high reduction (fuel-rich).

A significant finding from this work was that NO reduction does not appear to depend on overall stoichiometry so much as on the ratio of oxygen leaving the primary to the secondary fuel, i.e., relatively little secondary fuel injection in terms of overall stoichiometry may cause a significant reduction in NO.

Myerson suspected direct attack by hydrocarbon radicals on NO for NO reduction. The following reactions were suggested:

$CH + NO \rightarrow N + CHO$

$CH + NO \rightarrow HCN + O$

followed by either:

$N + NO \rightarrow N_2 + O$

$HCN \rightarrow HNCO \rightarrow NH \rightarrow NH_2 \rightarrow NO.$

Wendt et al. (1973) had proposed a reversed Zeldovich step to account for the initial NO attack:

$NO + O \rightarrow N + O_2$

However, this reaction does not appear to be sufficiently rapid to account for the results, and may even be driven backwards by N-atoms produced by the hydrocarbon - NO reaction.

Shaub and Bauer (1978) investigated the reaction of hydrocarbons, NO and C_2 in a single pulse shock tube. A model developed for their study indicated the importance to, and sensitivity of, the results of the rates of hydrocarbon fragments (CH, CH_2) with NO.

2.0 EXPERIMENTAL

Laboratory-scale experiments have been performed to verify the potential for in-furnace NO_x reduction by reburning and to investigate the effects of key parameters on the process. Sections are included in this discussion of the experimental phase to:

- State the specific goals of the experiments.
- Describe the setup and procedures.
- Discuss the results.
- Summarize the roles of important parameters.
- Recommend further experiments.

2.1 Goals

The experiments were designed to use existing equipment to provide a maximum of information in a limited time. To meet these criteria of speed and thoroughness, the experiments were performed in two phases using different systems.

The initial experiments were carried out in the FCR thermal decomposition reactor. The goals of these experiments were to:

- Demonstrate the viability of the reburning concept.
- Investigate the limits within which the concept works.
- Determine those areas of maximum interest for the more detailed studies.

The detailed studies utilized an adiabatic backfired flow reactor for maximum control of key parameters. These experiments, performed under controlled and well-documented conditions, were designed to provide useful information for the parallel analytical studies. The goals of the detailed studies were to:

- Investigate and separate the effects of key parameters:
  - Stoichiometry
  - Mixing
  - Temperature

- Provide mechanistic information as to the formation of intermediates such as NH_3 and HCN in the fuel-rich zone.
- Compare reburning and rich/lean staged combustion as alternative NO_x reducing techniques.

2.2 Setup

Figure 2-1 is a schematic of the initial experiments. The setup is similar to the one used by Wendt, Sternling, and Matovich (1973). The tests were carried out in the FCR thermal decomposition reactor which was modified to allow secondary fuel and air injection. The burner was operated as a lean CH_4 flat flame with either HCN or NH_3 doping. Secondary CH_4 was injected 2 inches (5.08 cm) below the burner using a tee with small holes drilled in the top of the tee as shown in the figure. In this manner the CH_4 was rapidly mixed across the burner flow, producing a sooty luminous reduction zone. Secondary air could be injected in a similar manner 5 inches (12.7 cm) below the burner. Primary flame temperature could be changed by varying the proportion of primary nitrogen, and secondary temperatures could be changed by varying the point of methane injection in the rapidly cooling reactor. Gas concentrations were measured using the EER emissions console with the following instrumentation:

- Thermo-Electron chemiluminescent NO-NO_x analyzer.
- Taylor paramagnetic O_2 analyzer.
- Beckman infrared CO and CO_2 analyzers.

Figure 2-2 shows the setup for the detailed measurements. The tests were carried out under approximately adiabatic conditions in a backfired flow reactor. A 2.25 inch (5.72 cm) ID alumina muffle tube separated the reaction zone from the propane/air backfired zone. The reaction zone was divided into primary, secondary, and tertiary stages to simulate reburning. Premixed primary reactants were introduced to the top of the reactor through a water-cooled stainless steel burner containing four 0.56 inch (1.41 cm) ID injector holes. Secondary fuel was injected radially 4.34 inches (11.03 cm) downstream through eight 0.043-inch (0.109 cm) holes drilled in the 0.5-inch (1.27 cm) OD stainless steel injector tube situated on the centerline of the reactor. Tertiary air was injected in a similar fashion 10 inches (25.4 cm)

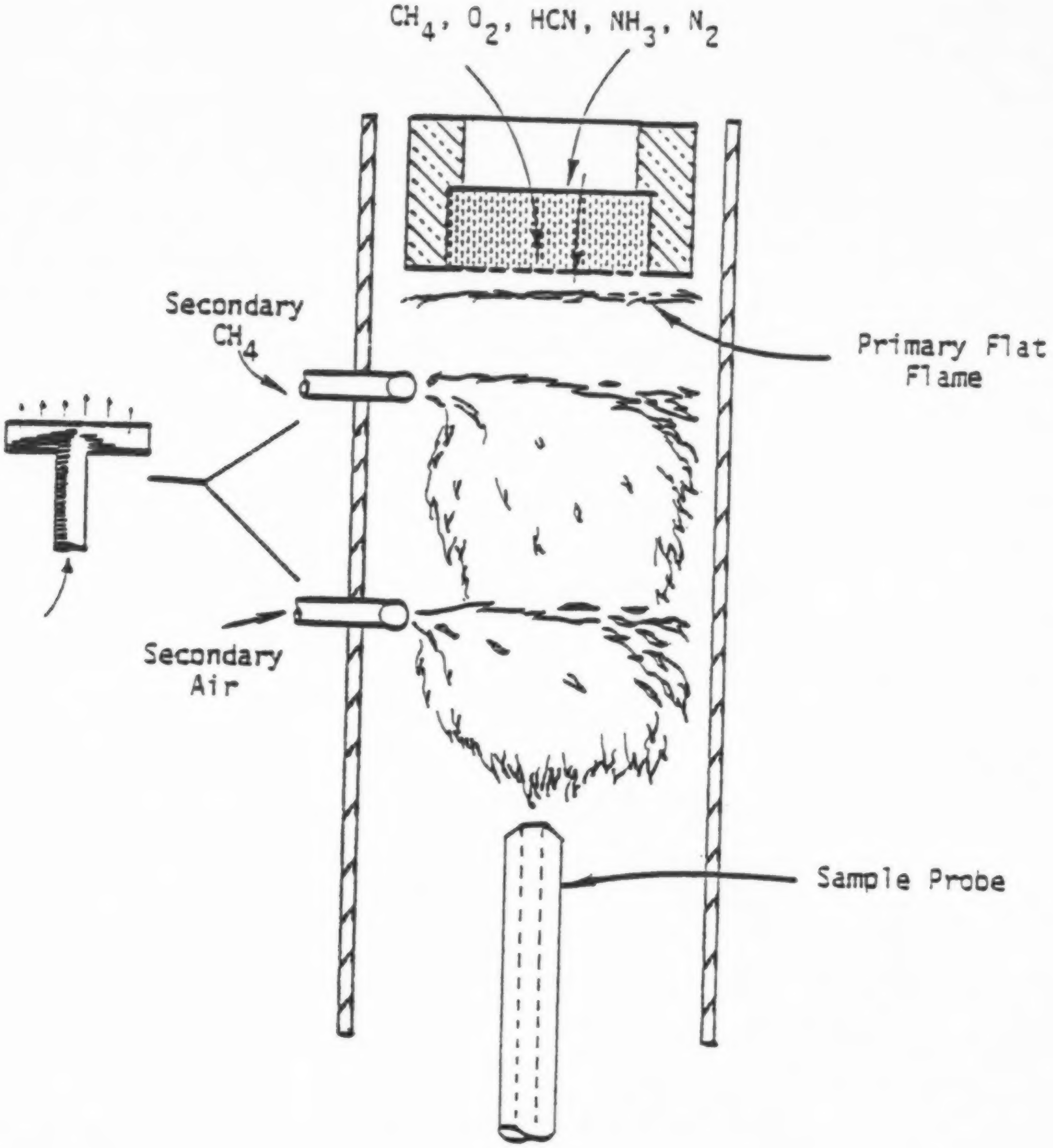

CH_4, O_2, HCN, NH_3, N_2
Secondary CH_4
Primary Flat Flame
Secondary Air
Sample Probe

Figure 2-1. Experimental Set-up for In-Furnace NO_x Reduction Preliminary Tests.

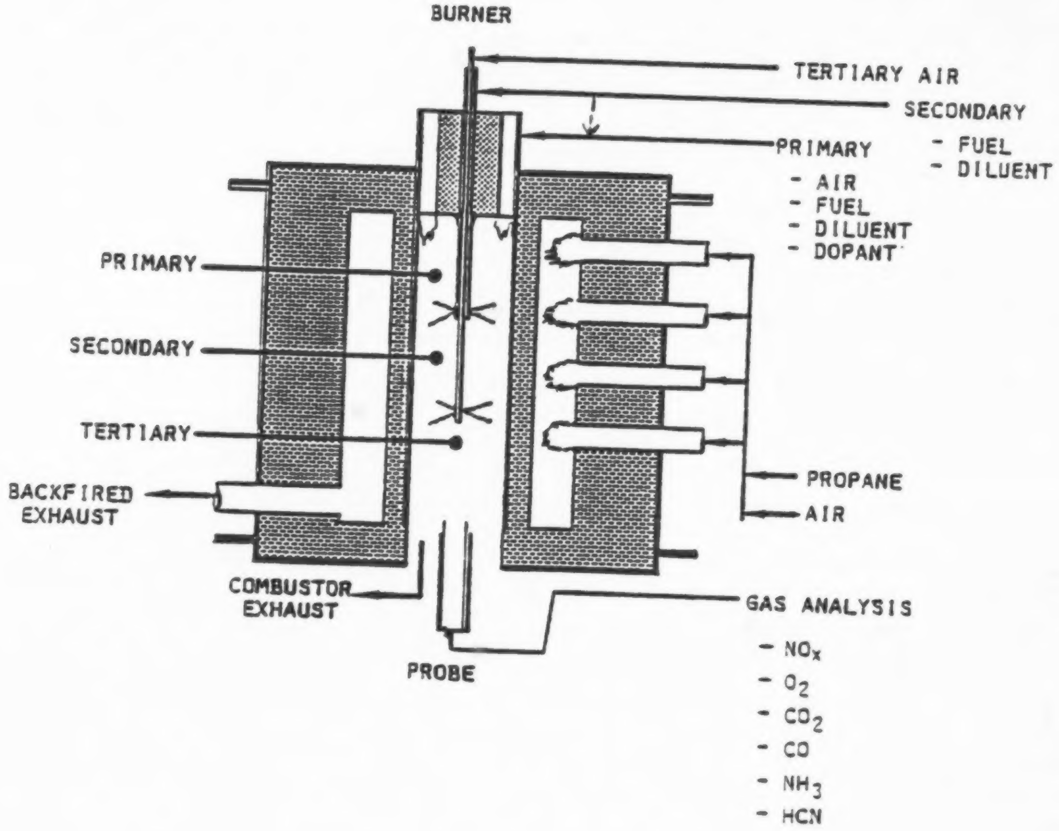

BURNER
TERTIARY AIR
SECONDARY
- FUEL
- DILUENT
PRIMARY
- AIR
- FUEL
- DILUENT
- DOPANT
PRIMARY
SECONDARY
TERTIARY
BACKFIRED EXHAUST
PROPANE
AIR
COMBUSTOR EXHAUST
GAS ANALYSIS
- NO_x
- O_2
- CO_2
- CO
- NH_3
- HCN
PROBE

Figure 2-2. In-Flame NO Reduction Backfired Reactor System.

further downstream. Both of the uncooled injector tubes were wrapped with ceramic paper to insulate the tubes and to prevent possible catalytic effects of hot stainless steel. Samples were taken through a water-cooled stainless steel probe situated 7.16 inches (18.19 cm) downstream of the tertiary air injector. Continuous measurements of NO, CO, CO_2, and O_2 were taken, using the emissions console described in the preceding paragraph. Batch samples of NH_3 and HCN were taken by bubbling a measured volume of combustion gas through a measured volume of distilled water and measuring NH_3 and HCN liquid concentration with Orion ion-specific electrodes.

Primary reactants consisted of air, methane as the hydrocarbon fuel, nitrogen as diluent to control flame temperature, and nitric oxide (in nitrogen) as the fuel nitrogen dopant. In the secondary, additional methane and nitrogen were added to the primary combustion products; and in the tertiary, air was added to complete the reburning process. Rotameters, calibrated for the appropriate gas and pressure with a dry test meter, were used to monitor the seven reactant flow streams.

Generally, experiments were run maintaining a constant NO flow to the primary of 0.05 SCFH (0.024 lpm) and a constant total (primary, secondary and tertiary) reactant flow of 100 SCFM (47.2 lpm), corresponding to a full dry conversion of NO in the tertiary of about 600 ppm. Adiabatic flame temperatures in the primary, secondary and tertiary were maintained approximately equal to the backheated wall temperature by controlling the flows of primary nitrogen, secondary nitrogen, and excess tertiary air; thus separating flame temperature from stoichiometry in the primary and secondary zones. Reburning was compared to rich/lean staged combustion by adding the secondary to the primary reactants in the primary burner.

All samples were taken from the bottom of the muffle tube. Secondary samples were taken by turning off the tertiary air, and primary samples were taken by turning off both the secondary and the tertiary streams. Thus primary and secondary residence times under sampling conditions were longer than primary and secondary residence times under typical three-stage reburning operation. Table 2-1 compares residence times for reburning and staged combustion under primary, secondary and tertiary sampling conditions for the

TABLE 2-1. BASELINE DATA POINT RESIDENCE TIMES

	PRIMARY SAMPLING	SECONDARY SAMPLING	TERTIARY SAMPLING
PRIMARY RESIDENCE TIME (ms)	476	96	96
SECONDARY RESIDENCE TIME (ms)	---	379	221
TERTIARY RESIDENCE TIME (ms)	---	---	127

Reburning
1100°C

110% T.A. Primary
90% T.A. Secondary
125% T.A. Tertiary

	PRIMARY SAMPLING	SECONDARY SAMPLING
PRIMARY RESIDENCE TIME (ms)	475	317
SECONDARY RESIDENCE TIME (ms)	---	127

Rich/Lean Staging
1100°C

90% T.A. Primary
125% T.A. Secondary

baseline reburning data point of 110-percent theoretical air primary, 90-percent theoretical air secondary, 125-percent theoretical air tertiary, 1100°C adiabatic flame temperature; and the corresponding staged data point of 90-percent theoretical air primary, 125-percent theoretical air secondary, 1100°C.

2.3 Results

The experimental results will be discussed in three sections:

- Initial experiments (reactant stoichiometry and temperature).
- Detailed measurements.
- Impact of nitrogen content of the reburning fuel.

The initial experiments utilized the FCR thermal decomposition reactor to demonstrate in-furnace NO_x reduction by reburning and to investigate the limits of applicability of the process. Preliminary experiments utilizing the back-fired reactor were used to investigate trends of NO_x reduction by reburning. Problems with the oxygen measurements and small air leaks (up to 10-percent of primary air) into the reactor made stoichiometric and adiabatic flame temperature calculations suspect. Thus, these tests were useful for examining the relative effects of a single variable within a single test run, but absolute comparisons of specific data points from different test runs were of little value due to a possible 10-percent error in stoichiometry. In the detailed measurements, accurate oxygen and CO_2 readings were used to calculate air leakage by mass balance; thus, absolute or "hard" data were obtained in these experiments.

2.3.1 Initial Experiments

The initial experiments examined the impact of secondary methane injection and primary oxygen concentration on NO_x reduction in reburning.

The influence of secondary methane injection is shown in Figure 2-3. The primary flame was operated at two different stoichiometries with different nitrogen diluent levels in order to hold the flame temperature constant. The doping was with HCN in nitrogen which yielded approximately 450 ppm NO. From this initial value, the NO was found to decrease to 200 ppm with 5 SCFH (2.4 lpm) of secondary fuel addition with a corresponding increase in CO to levels above 6 percent. The fractional decrease in NO was strikingly similar

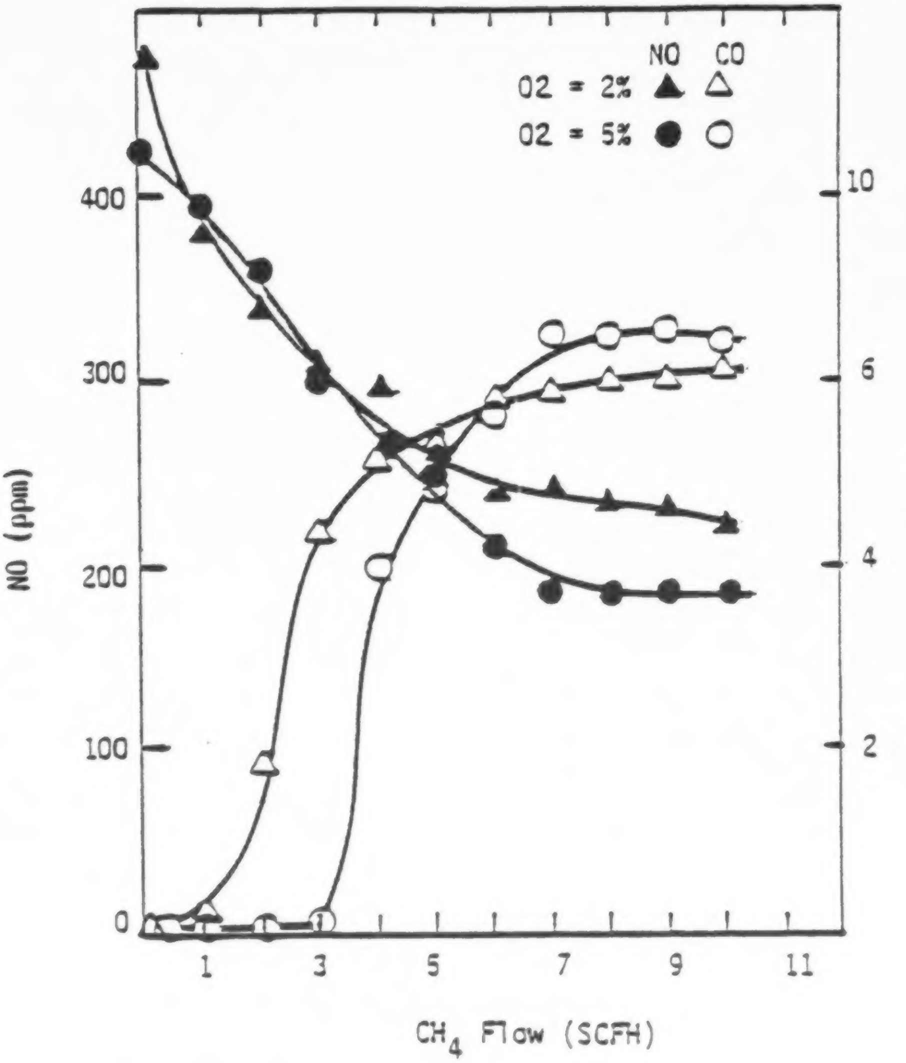


Figure 2-3. Impact of Secondary Methane Injection on NO and CO.

to the Wendt et al results at much higher levels of initial NO. If the secondary methane injection position was moved further from the burner, effectively lowering the reaction zone temperature due to the flow heat loss, the percent-reduction was dramatically decreased. For example, at 5 inches (12.7 cm) below the burner at which point the temperature had dropped approximately 150°C, the maximum reduction achievable was found to be 35 percent compared to 60 percent at higher temperature.

The effect of secondary methane injection on a variety of first-stage stoichiometries and NO levels is shown in Figure 2-4. The data were all taken at a constant flame temperature by adjusting the nitrogen diluent flow rate. Except at excessively high O_2 levels, the reduction was found to be somewhat insensitive to either the primary stoichiometry (as long as sufficient secondary fuel was added to change to a rich reduction zone) or initial NO concentration. These results were also in agreement with the early results of Wendt et al.

The secondary addition of air was also attempted at three different levels of secondary methane injection. Because of the lower temperatures in the burnout zone, it was not possible to burnout CO completely. However, the CO could be decreased by 90 percent to levels below 0.5-percent without significant increases in NO.

Results of these initial tests indicated the relative unimportance of primary zone excess oxygen and NO levels, and the strong impact of flame temperature on fractional NO reduction by injection of a hydrocarbon fuel into fuel-lean combustion products. These results pointed to important areas for further investigation in an adiabatic reactor:

- Independent study of second-stage temperature and stoichiometry effects.
- Investigation of the parameters which affect carbon burnout (CO concentration) after tertiary air addition.
- Formation and subsequent processing of intermediate species such as NH_3 and HCN.
- The impact of mixing on NO reduction and on tertiary CO burnout.

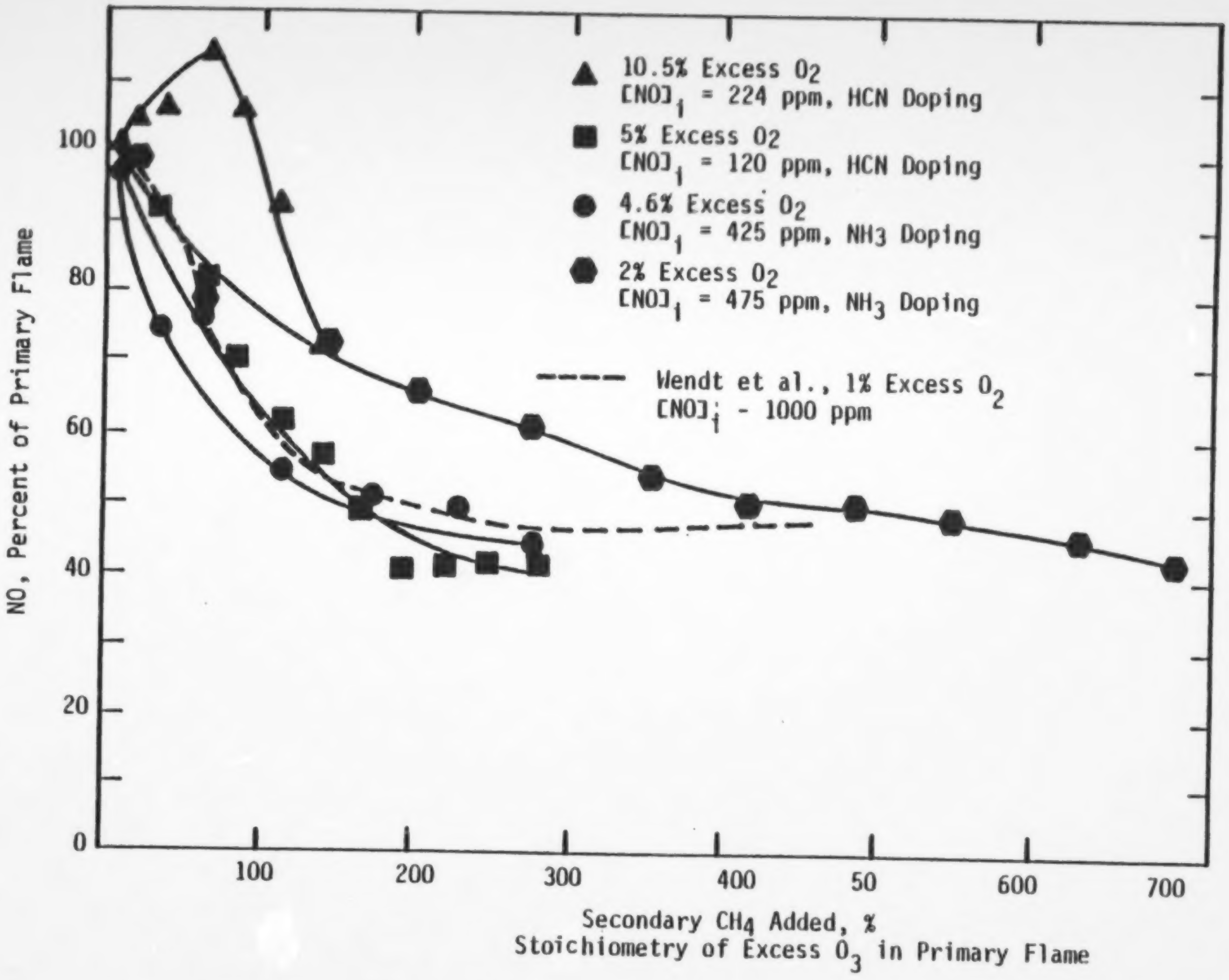


Figure 2-4. Impact of Primary Stage Excess Oxygen on NO_x Reduction.

2.3.2 Investigation of Trends

Experiments were performed to examine the effects of stoichiometry and mixing on NO_x reduction in reburning and in simple staged combustion. These experiments were performed against a backheated reactor wall temperature of 1100°C. Secondary temperatures (uncorrected for radiation loss) were measured with a bare fine-wire B-type (platinum 6-percent-rhodium vs. platinum 30-percent-rhodium) thermocouple; these measured temperatures were always between 1030° and 1150°C.

Figure 2-5 shows the effects of reburning on NO concentrations in the primary, secondary and tertiary stages. Approximately 80 percent of the reactant NO remained in the form of NO in the fuel-lean premixed primary stage. Subsequent experiments showed NO conversion in the lean primary to be generally closer to 80 percent. NO_x measurements did not differ significantly from NO, showing that negligible amounts of NO_2 were formed in the primary. Injection of additional fuel in the form of methane caused NO concentration to drop steadily with decreasing secondary stoichiometry (the ratio of primary air to the amount of air required for complete combustion of primary and secondary fuel) to a conversion level of about 20 percent at a secondary stoichiometry of around 75 percent theoretical air. NO conversion levels at this 75 percent theoretical air secondary data point increased to around 45 percent with the introduction of sufficient tertiary air for fuel-lean burnout, suggesting the presence of partial combustion products such as NH_3 or HCN in the secondary.

This variable secondary stoichiometry experiment was repeated, and batch samples were taken for specific ion NH_3 and HCN measurements. The results, shown in Figure 2-6, indicated significant formation of HCN with decreasing secondary stoichiometry. Total fixed nitrogen concentrations did not change much with increased secondary fuel injection, as the decrease in NO was balanced by the increase in HCN. As a result, NO concentrations in lean tertiary burnout were not a strong function of secondary stoichiometry. In general, about 20 percent of the injected NO was reduced to N_2 in the fuel-lean primary, about 25 percent of the remaining NO was reduced to N_2 in the fuel-rich secondary, and about 20 percent of the remaining XN was reduced to N_2 in the fuel-lean tertiary. Thus, each stage contributed to XN reduction. It should be noted that secondary stoichiometry was controlled in these tests

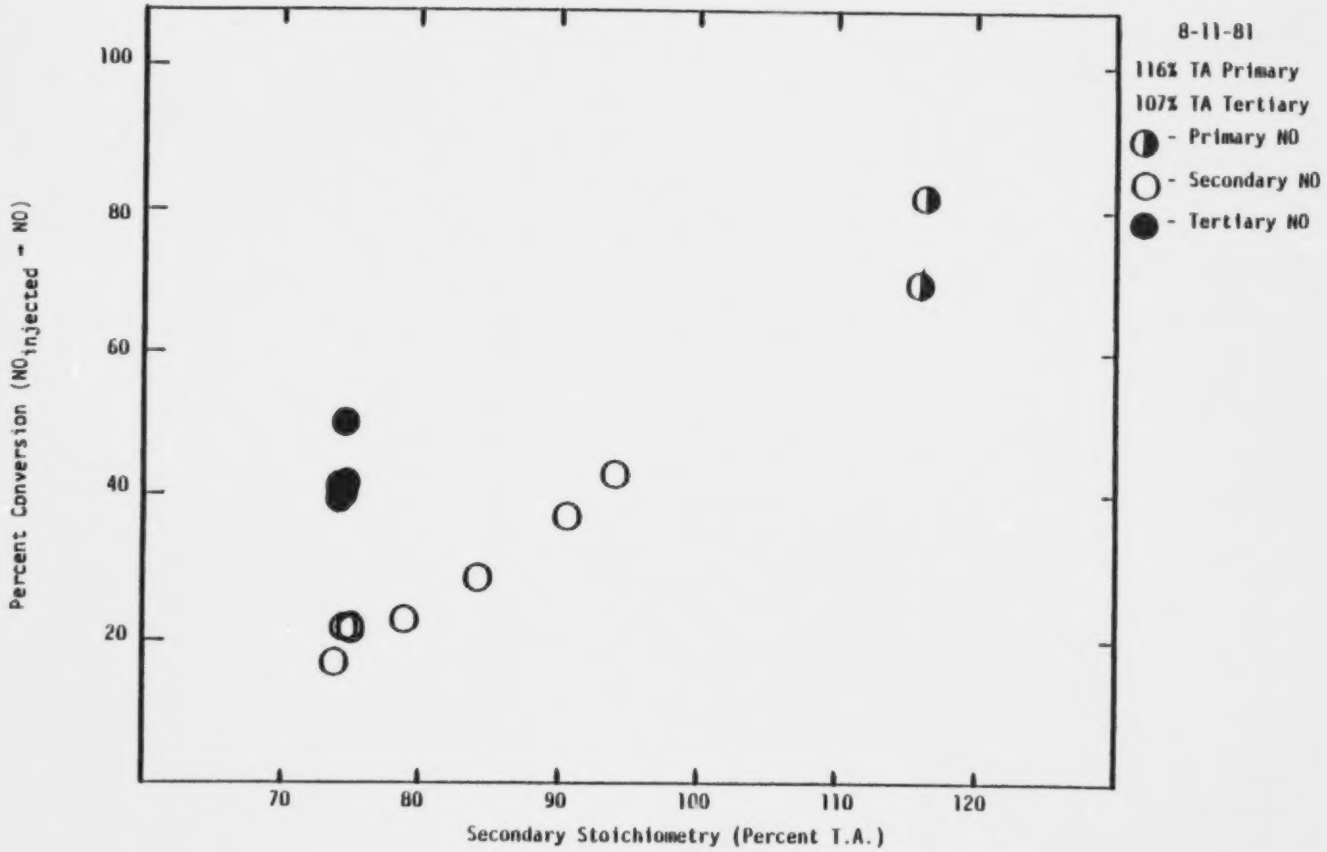


Figure 2-5. Effect of Secondary Stoichiometry on Secondary and Tertiary NO in Reburning.

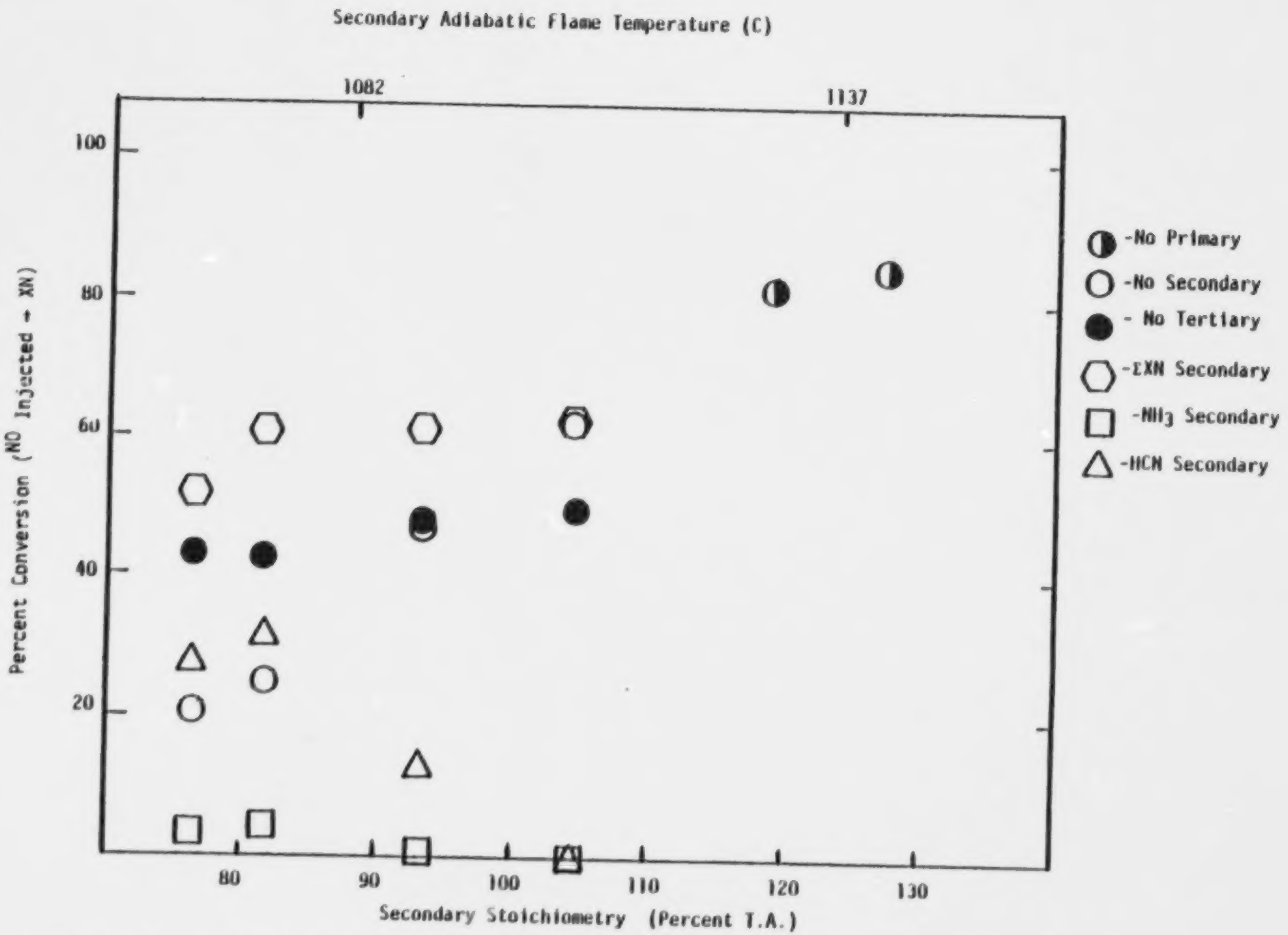


Figure 2-6. Effect of Secondary Stoichiometry on Secondary XN and Tertiary NO in Reburning.

by varying only the secondary methane flow; thus, adiabatic flame temperature in the secondary, and stoichiometry and adiabatic flame temperature in the tertiary, varied with secondary stoichiometry.

Similar results were achieved by injecting additional secondary methane into fuel-rich primary combustion products as shown in Figure 2-7. In this case, a greater proportion of the injected NO was reduced in the primary (operated at 92 percent theoretical air), and a lesser proportion was reduced in the richer secondary and lean tertiary; but the ultimate results were quite similar: minimum overall conversion levels of about 40 percent of injected NO occurred at secondary stoichiometries between 75 and 80 percent theoretical air.

To further investigate the relative effects of primary and secondary stoichiometry, a test was performed maintaining total methane flow constant, but varying the proportions of the total which went to the primary and the secondary. Thus, secondary stoichiometry was maintained at a constant 74 percent theoretical air, but primary stoichiometry was varied from 116 to 91 percent theoretical air. Figure 2-8 shows the results of this test. Conversion of injected NO to tertiary NO remained at a constant 40 percent, independent of primary stoichiometry so long as the secondary stoichiometry remained at 74 percent theoretical air. Secondary NO concentrations were also unaffected by primary stoichiometry.

As primary stoichiometry appeared to have no effect on NO reduction by reburning, it was decided to eliminate the fuel-lean stage entirely. This was accomplished by adding the secondary fuel to the primary reactants, changing the reburning reactor into a rich/lean staged combustor. Results of variable primary staged stoichiometry tests (corresponding to variable secondary reburning stoichiometry tests) are shown in Figure 2-9. The trends were the same as those observed in similar reburning tests (Figure 2-6). NO decreased with decreasing rich-stage stoichiometry while HCN and, to a lesser extent, NH_3 increased. Minimums for primary ΣXN and for secondary NO occurred at a rich-stage stoichiometry of around 80 percent theoretical air. These values appeared to be more sharply dependent upon stoichiometry than in the corresponding reburning tests, perhaps due to the longer fuel-rich residence time.

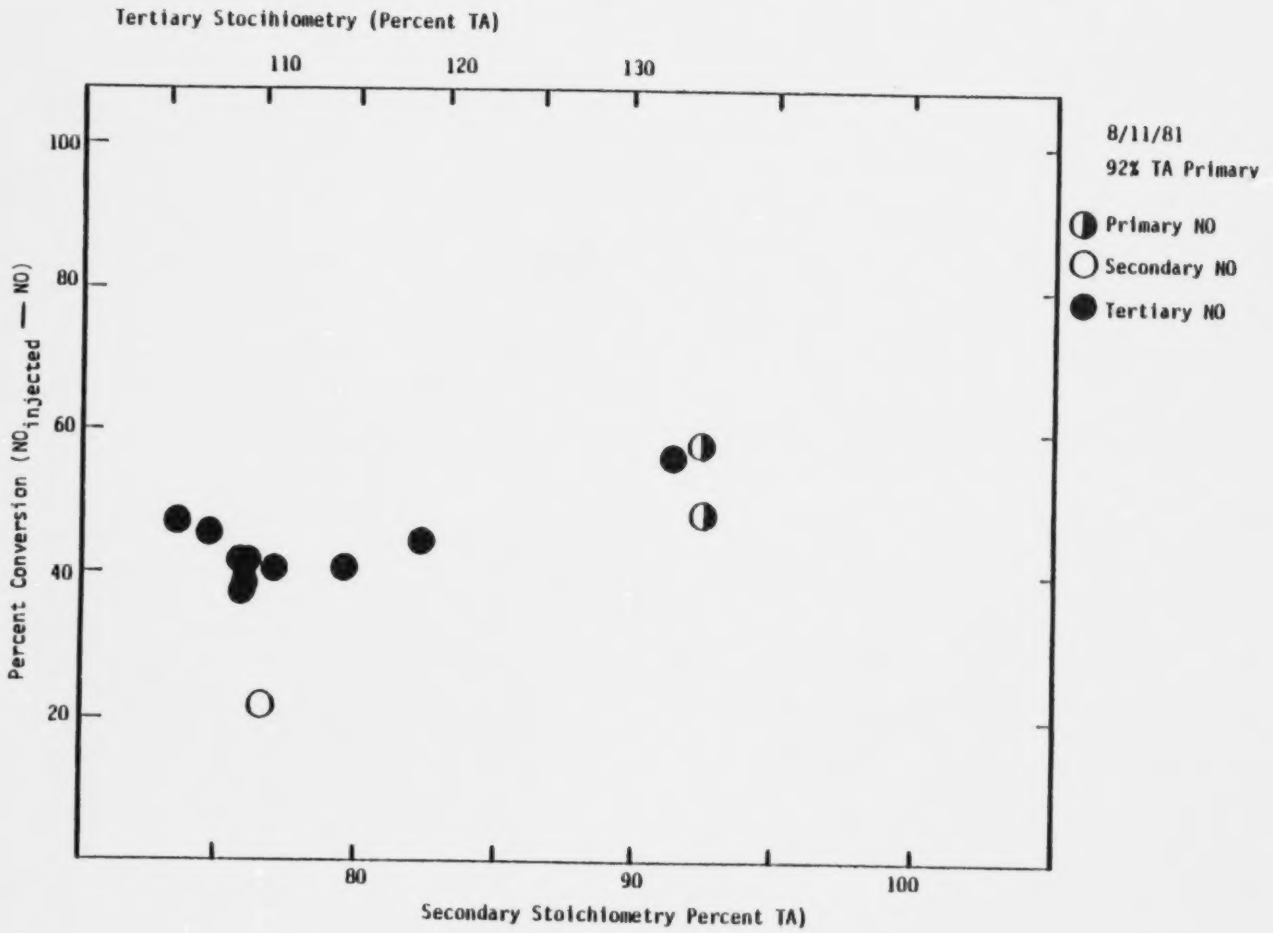


Figure 2-7. Effect of Secondary Stoichiometry on Tertiary NO in Rich Primary Reburning.

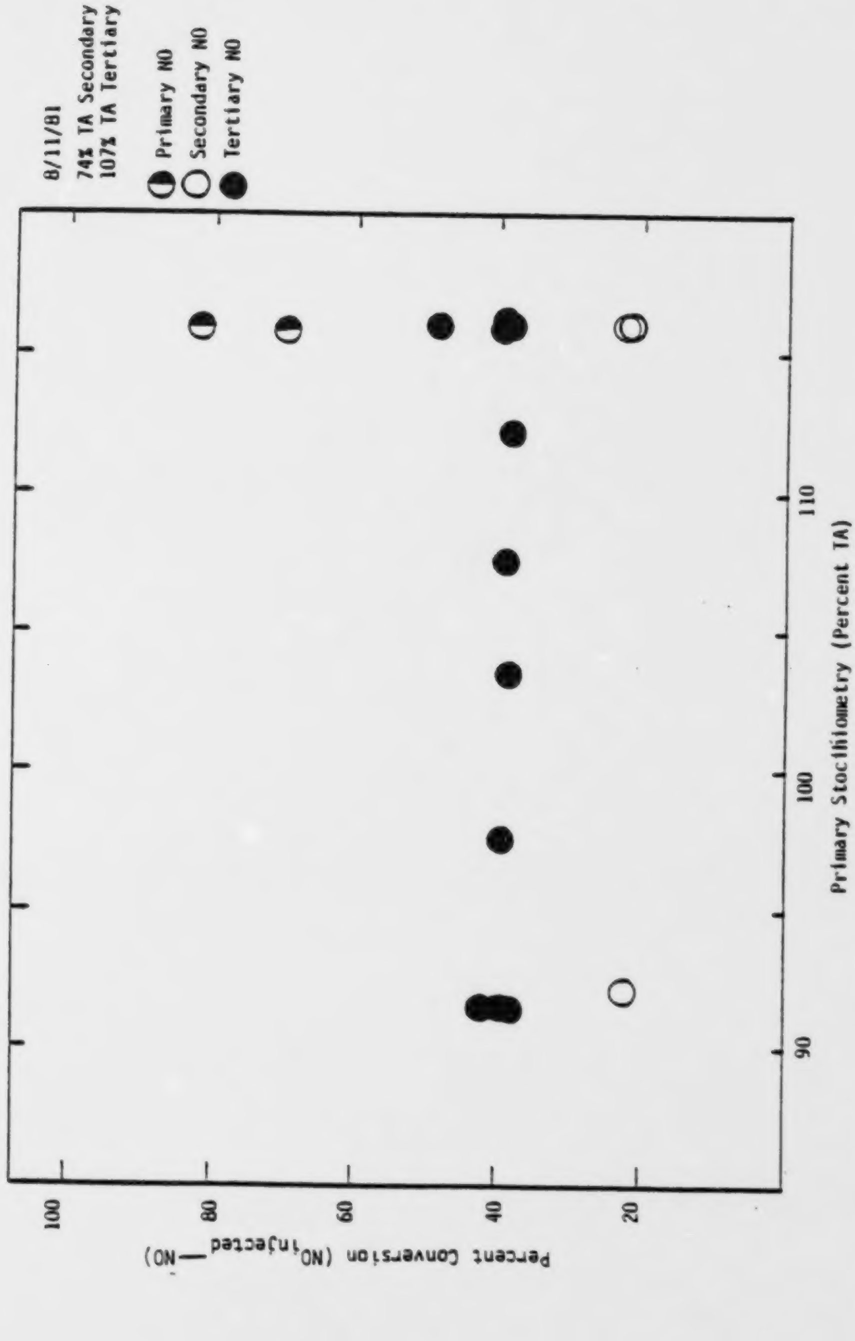


Figure 2-8. Effect of Primary Stoichiometry and Secondary NO in Reburning.

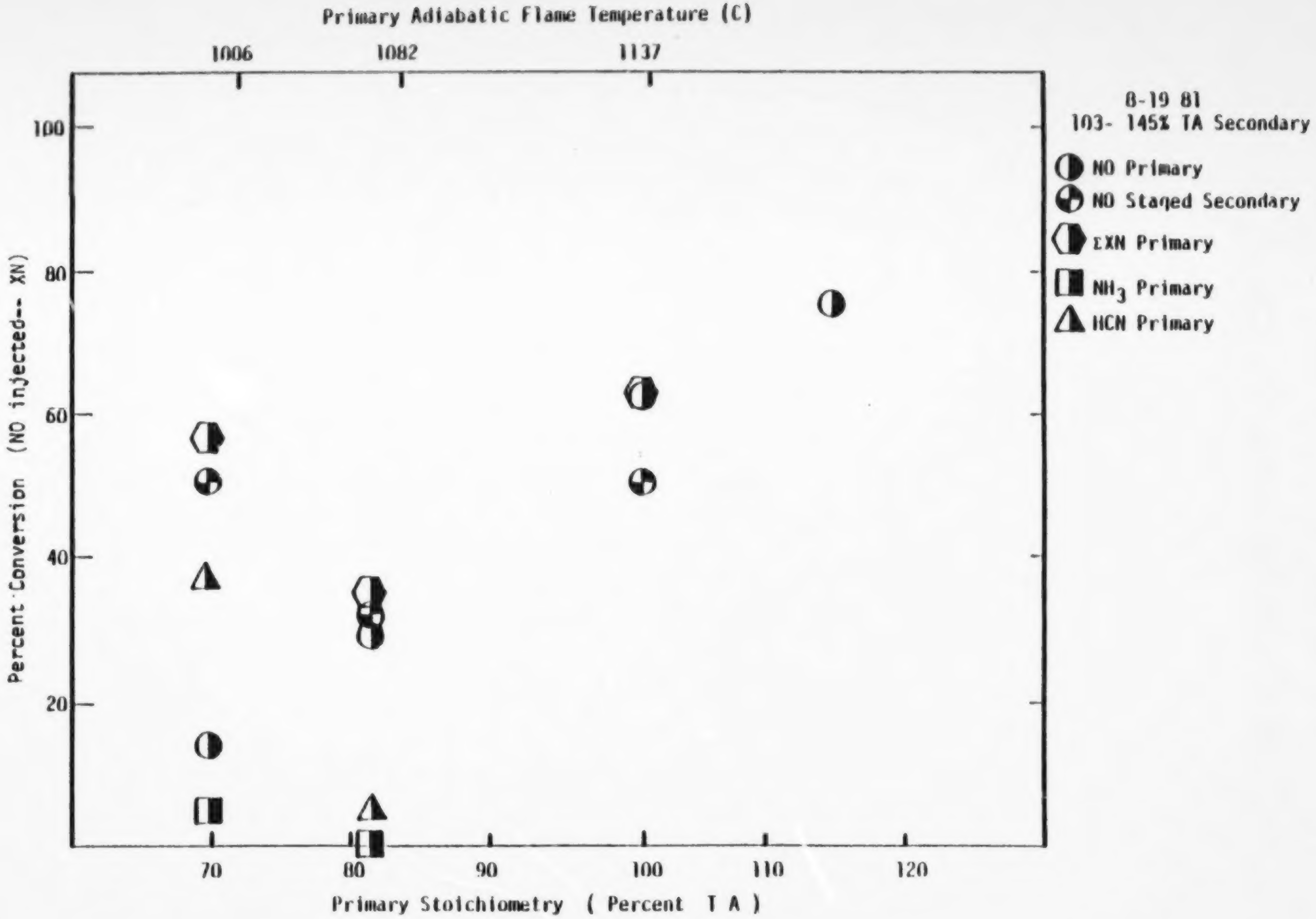


Figure 2-9. Effect of Primary. Stoichiometry on Primary XN in Staged Combustion.

Effects of tertiary stoichiometry in reburning were investigated by varying the tertiary air flow. Figure 2-10 shows that NO increased and CO decreased with increasing tertiary air. This suggests that NO reduction is improved by incomplete combustion and that a trade-off between the production of different pollutants must be considered in optimization of the technique.

Secondary mixing effects in reburning were examined by varying the nitrogen flow to the secondary. Figure 2-11 shows that increasing the secondary injection velocity (cold) from 150 to 400 cm/sec (corresponding to a decrease of 30°C in secondary adiabatic flame temperature) caused a slight increase in secondary NO and a slight decrease in tertiary NO. Tertiary CO remained below 100 ppm at all injection velocities although CO concentrations appeared higher at the increased velocities. Figure 2-12 shows similar results for the test repeated including NH_3 and HCN measurements in the secondary. No significant trends were observed in the behavior of these nitrogenous intermediates.

2.3.3 Detailed Measurements

In the detailed measurements, oxygen and carbon dioxide concentrations in fuel-lean combustion were carefully monitored. These concentrations were used in a mass balance to estimate air leakage into the reactor due to the slight vacuum induced by the exhaust blower. This leakage varied with operating conditions to a maximum of 10 percent of primary air. Care was also taken to maintain the adiabatic flame temperature very close to the backheated wall temperature in order to completely separate temperature and stoichiometry effects. These tests re-examined the effects of secondary stoichiometry, compared reburning and rich/lean staged results under more carefully controlled conditions, and investigated the effects of adiabatic flame temperature on NO reduction by reburning.

Figure 2-13 shows the effect of secondary stoichiometry on the concentrations of nitrogenous species in the secondary and on tertiary NO concentrations. The adiabatic flame temperature of all three stages was maintained at 1100°C by varying the amount of N_2 diluent added to the primary and the secondary, and by varying the excess air added to the tertiary. Primary stoichiometry was maintained at 110 percent theoretical air except for the richest secondary data point where it was necessary to go to 120 percent primary theoretical air to maintain secondary adiabatic flame temperature at

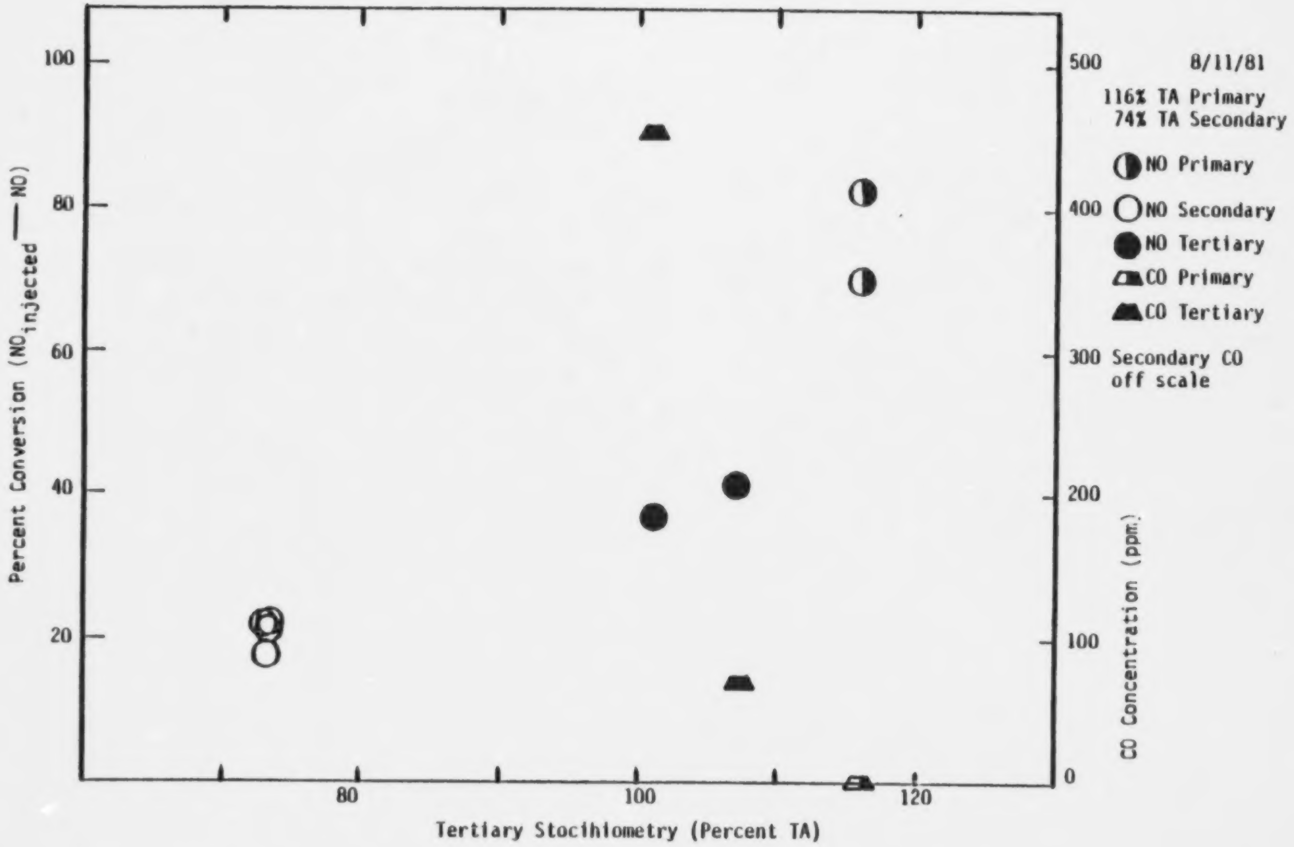


Figure 2-10. Effect of Tertiary Stoichiometry on Tertiary NO and CO in Reburning.

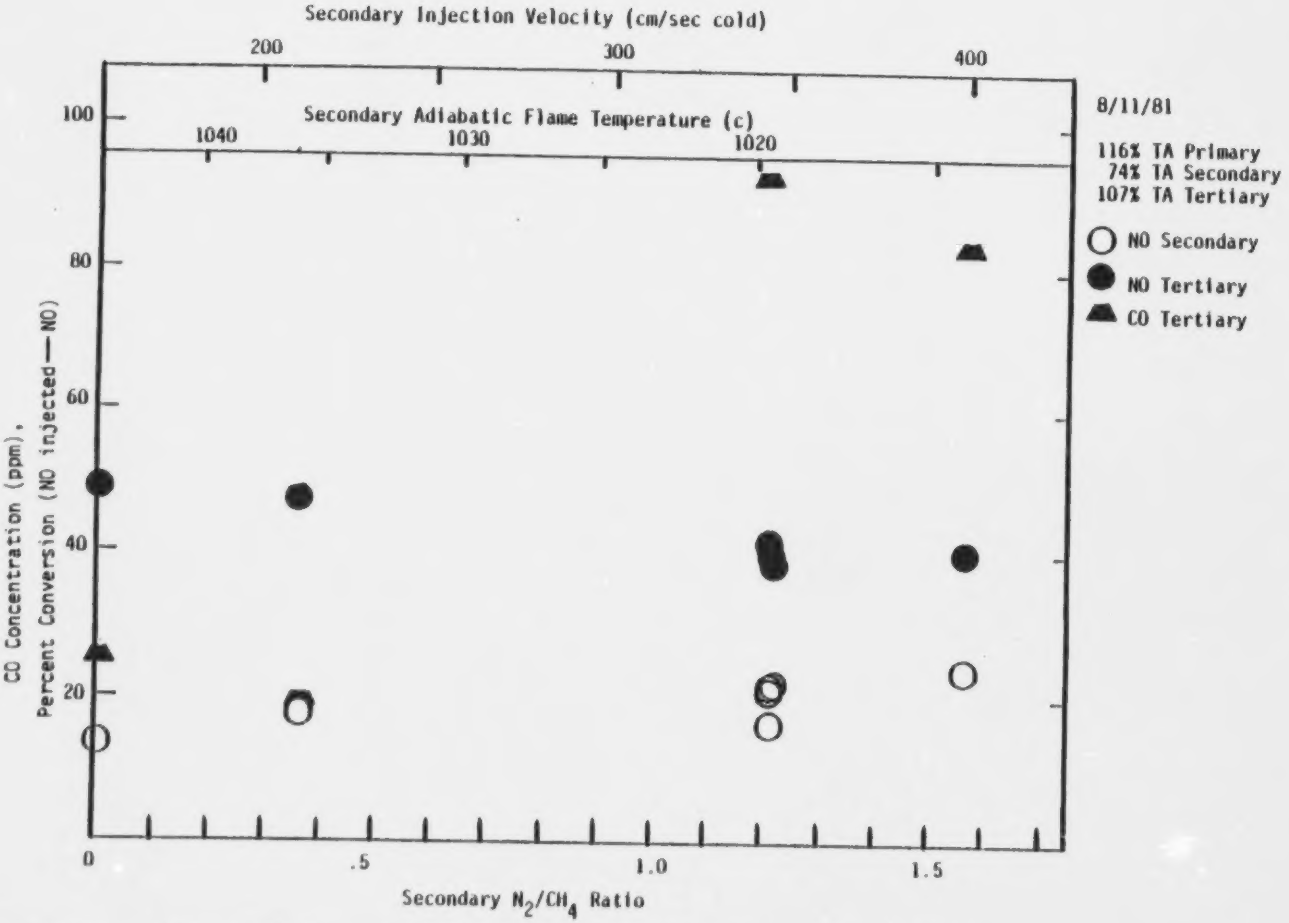


Figure 2-11. Effect of Secondary Injection Velocity on Secondary NO and Tertiary NO and CO in Reburning.

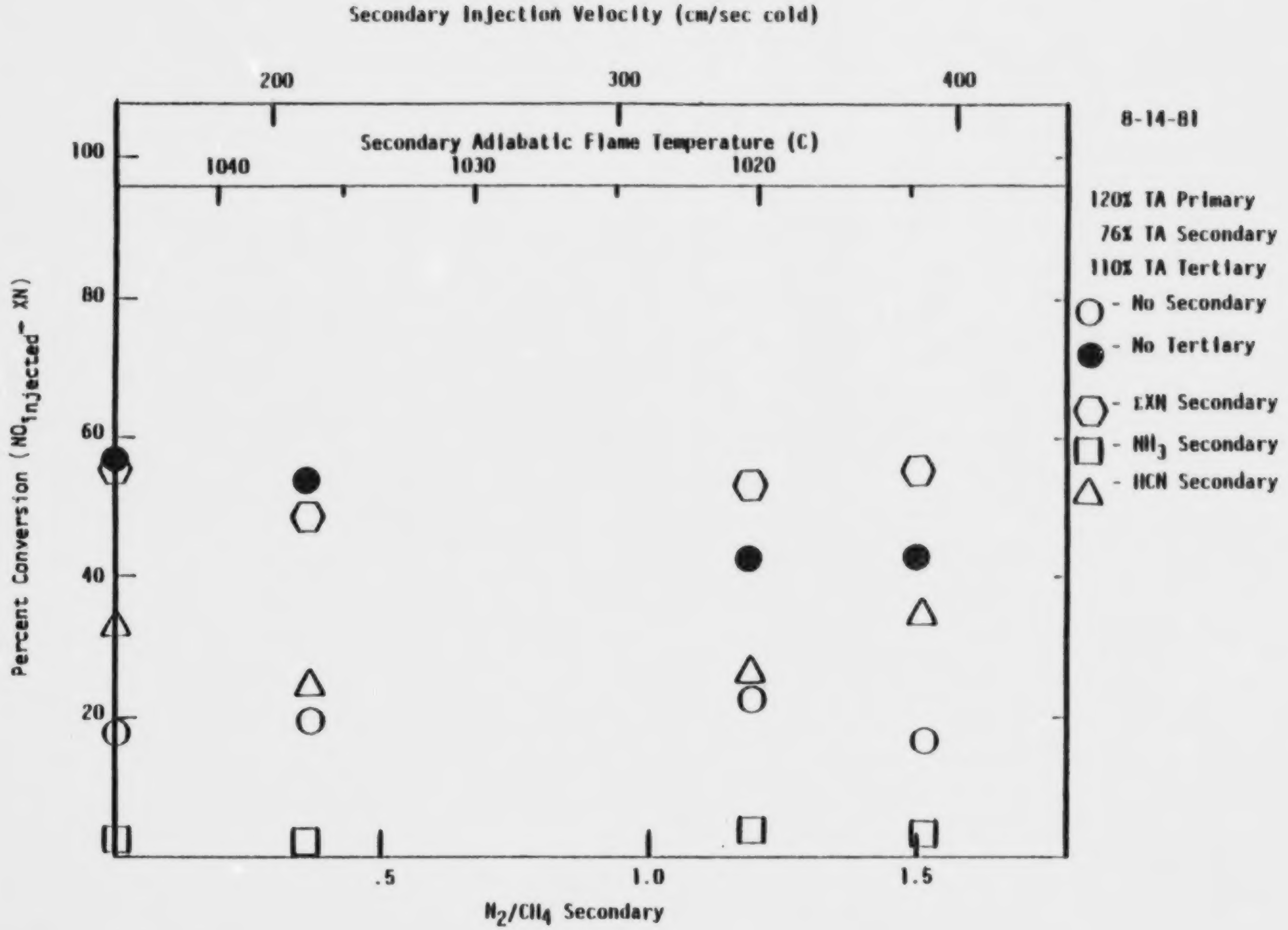


Figure 2-12. Effect of Secondary Injection Velocity on Secondary XN and Tertiary NO in Reburning.

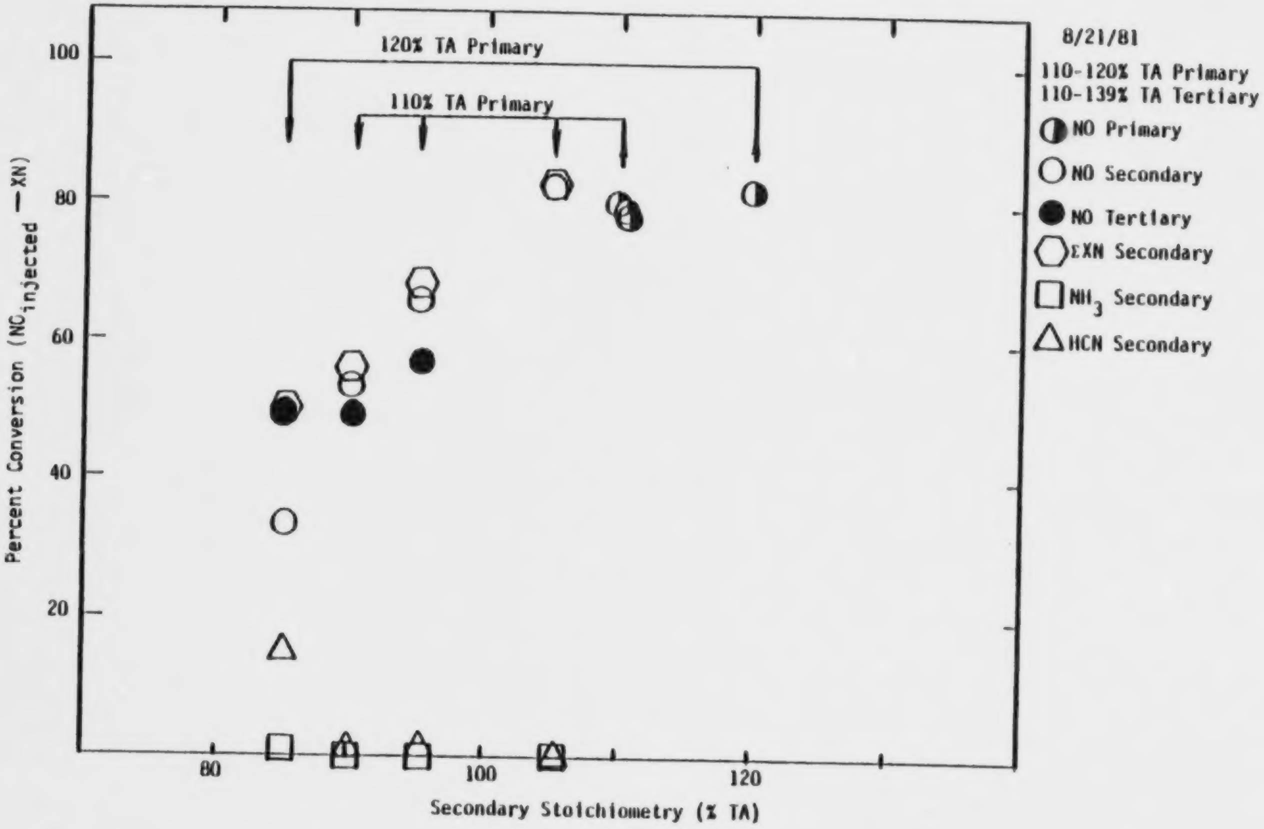


Figure 2-13. Effect of Secondary Stoichiometry on Secondary XN and Tertiary NO in Reburning.

1100°C. Conversion of injected NO to primary NO was consistently around 80 percent. Secondary NO decreased with decreasing secondary stoichiometry while secondary HCN increased, becoming significant at a secondary stoichiometry of 85 percent theoretical air. At this point, secondary HCN and tertiary NO appeared to reach a minimum of 50 percent of injected NO or 62 percent of primary NO. Richer secondary data points were impractical due to the necessity of burning very lean primaries to maintain the same secondary adiabatic flame temperature.

A three-way valve was placed in the secondary reactant line allowing the secondary reactants to be diverted to the primary stream facilitating a direct comparison of reburning with rich/lean staged combustion at identical rich stage stoichiometries. Figure 2-14 shows the results of such a comparison at variable rich-stage stoichiometries. The staged results paralleled the reburning results, but yielded slightly lower conversions of injected NO to burned out NO at all rich stage stoichiometries, possibly due to the increase in rich residence time gained by utilizing the primary as the rich burner and maintaining the tertiary air injector as the lean burner.

Figure 2-15 shows a similar comparison at variable adiabatic flame temperature. In these tests, the rich stage stoichiometry was maintained at a constant 90 percent theoretical air. The backheated wall temperature was maintained equal to the adiabatic flame temperature which was controlled by varying the amount of nitrogen diluent added to the reburning primary and secondary (staged primary) stages and the amount of excess air added to the reburning tertiary (staged secondary) stage. Conversion of injected NO to burned out NO decreased with increasing adiabatic flame temperature for both reburning and staged combustion, although temperature appeared to have a greater effect on staged combustion than on reburning. Figure 2-16 shows that NH_3 and HCN concentrations in the 90 percent theoretical air secondary remained low at adiabatic flame temperatures between 900° and 1100°C.

2.4 Summary

Reburning has been demonstrated to be a viable concept for NO_x reduction. It provides significant but not spectacular reductions of NO over a wide range of operating conditions and is relatively insensitive to stoichiometry and mixing; however, NO reduction in reburning is significantly enhanced at

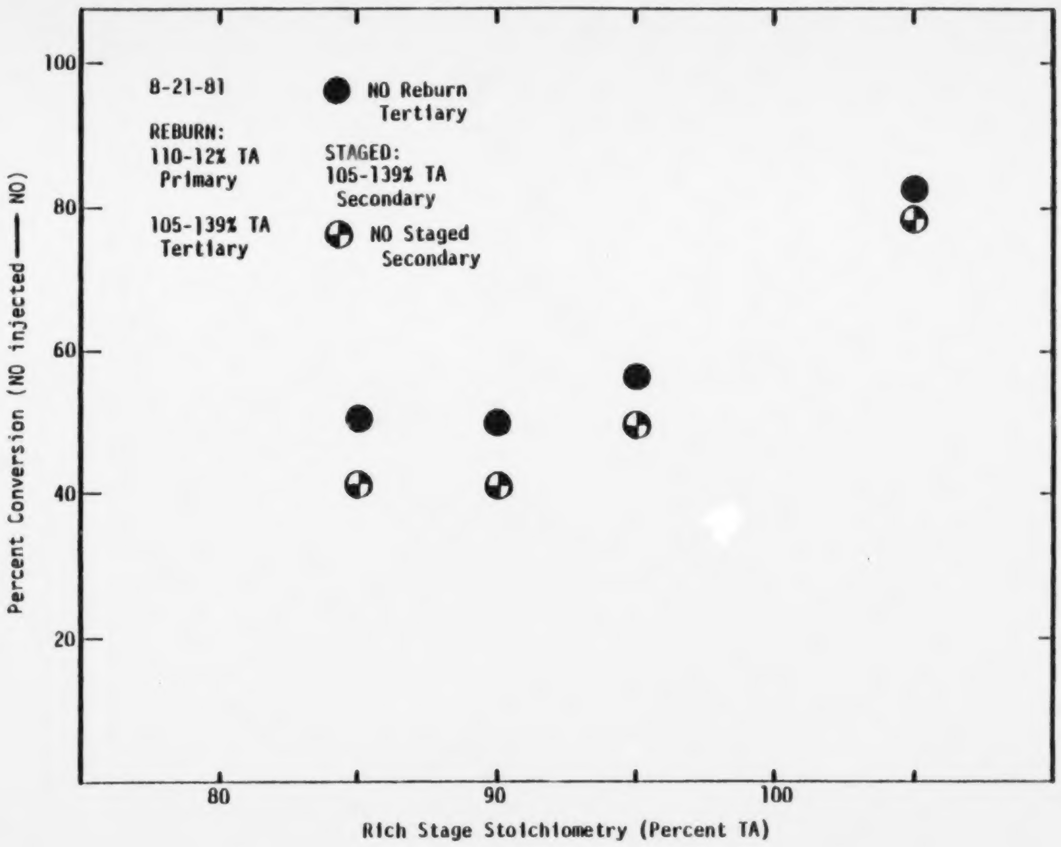


Figure 2-14. Staged/Reburning Comparison - Effect of Rich Stage Stoichiometry.

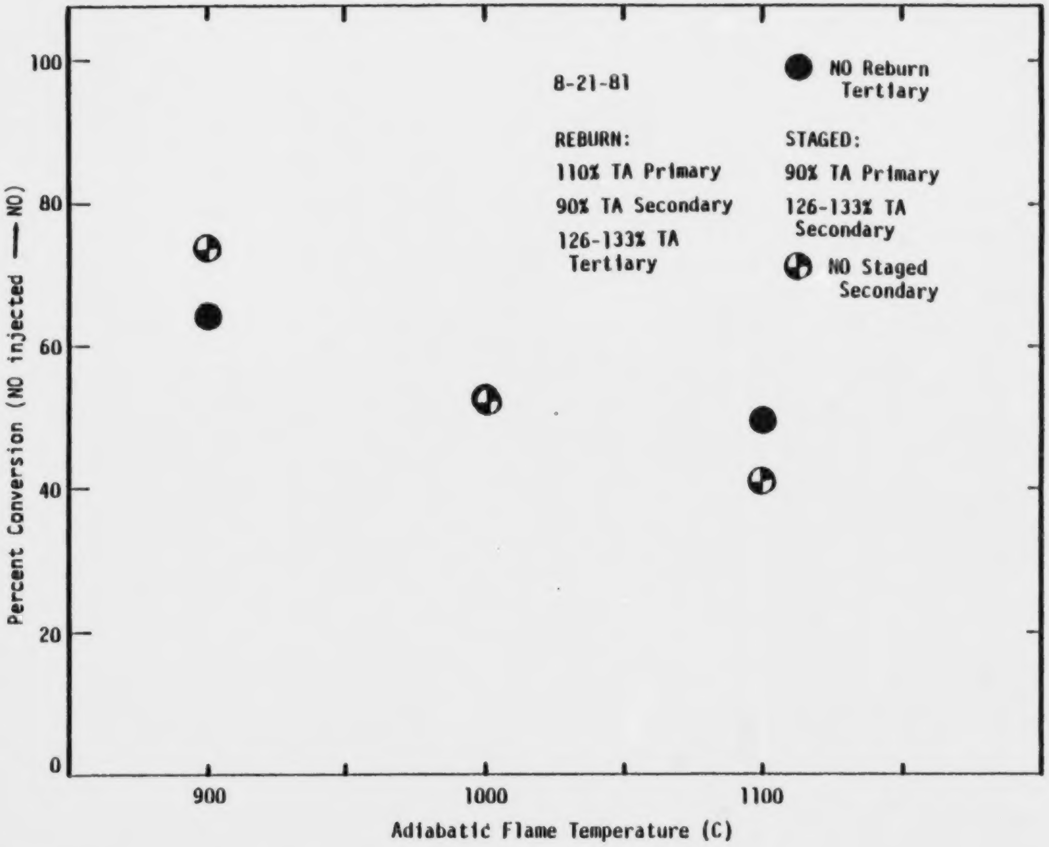


Figure 2-15. Staged/Reburning Comparison - Effect of Adiabatic Flame Temperature.

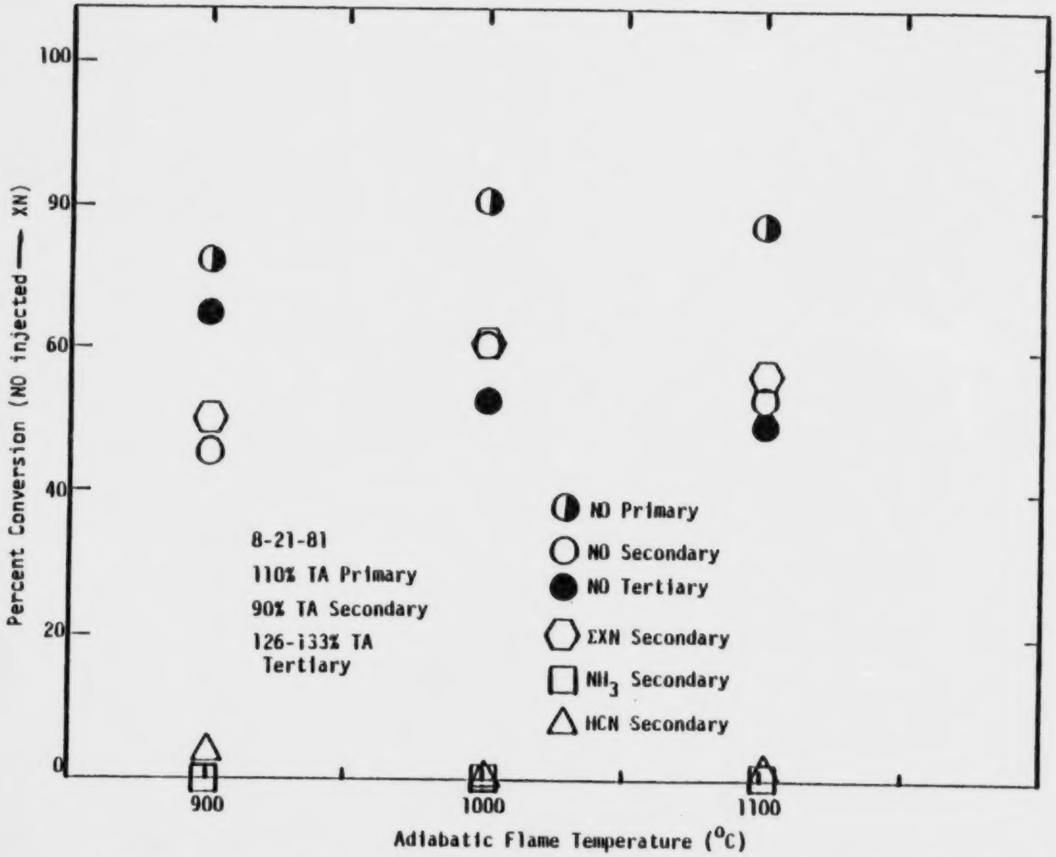


Figure 2-16. Effect of Adiabatic Flame Temperature on Secondary XN and Tertiary NO in Reburning.

higher temperatures. Reburning does not appear to incorporate any revolutionary new mechanisms for XN reduction. It is simply a means of increasing the residence time of combustion products under optimum XN-reducing conditions (high temperature fuel-rich combustion). There is no inherent advantage of reburning over rich/lean staged combustion with respect to NO reduction, although there may be operational advantages in coal combustion such as improved carbon burnout.

2.4.1 Parametric Effects

Effects of stoichiometry, mixing and temperature were investigated. Stoichiometry effects were investigated at temperatures between 1000° and 1150°C. Primary stage stoichiometry was unimportant; the stoichiometry of the fuel-rich secondary stage appeared to be the controlling factor. Optimum results were achieved at secondary stoichiometries between 75 and 90 percent theoretical air. Increased secondary mixing appeared to slightly enhance NO reduction in reburning, perhaps due to an effective increase in fuel-rich residence time. Increased secondary temperature significantly increased NO reduction in reburning. Residence time, a fourth parameter not directly investigated, appeared to have a significant effect on NO reduction. Conditions which indirectly contributed to longer fuel-rich residence times generally increased NO reduction.

2.4.2 Mechanistic Effects

Mechanistically, as previously observed, it appears that low temperatures enhance NO reduction in fuel-lean combustion, and high temperatures enhance NO reduction in fuel-rich combustion. As the fuel-rich stoichiometry becomes richer, NO decreases and HCN increases, balancing at a stoichiometry between 75- and 90-percent theoretical air; NH_3 parallels HCN, but remains at much lower concentrations.

2.5 The Impact of Reburning Fuel Nitrogen Content

Experiments were run to investigate the effects of the following parameters on NO reduction by reburning:

- Secondary stoichiometry
- Temperature

- Primary NO concentration
- Secondary fuel-nitrogen content

In addition, formation of intermediate fixed-nitrogen species in the secondary was studied and total fixed-nitrogen removal was compared in the secondary and tertiary stages.

Table 2-2 lists the test conditions for each experiment and the figure to which the conditions apply. Generally, the ratio of tertiary NO to primary NO is plotted against the test variable. The NO concentrations are corrected for dilution, thus ratio (or, more corrently, 100 percent minus this ratio) is a direct measure of the effective NO removal by reburning. In most cases, results for the fuel-nitrogen-containing secondary fuel (shaded points) are compared with results for the fuel-nitrogen-free secondary fuel (open points).

The first test run, shown in Figure 2-17, shows the effects of secondary stoichiometry on tertiary-to-primary NO ratio with and without secondary fuel nitrogen at low primary NO concentrations and relatively low temperatures. If the primary fuel had contained 0.5-percent fixed nitrogen, the measured 75 ppm NO concentration would correspond to a primary fuel-nitrogen conversion level of about 2.1 percent. The open points in the figure show that, even in the absence of secondary fuel-nitrogen, NO levels were only slightly lowered when reburning was applied to an already low NO_x primary: approximately 88 percent of the primary NO passed through to the tertiary when reburned at the optimum secondary stoichiometry of 90 percent theoretical air. The shaded points show that when the secondary fuel contained 0.5-percent fuel-nitrogen in the form of ammonia, NO emissions actually increased with reburning. The increase was greater at richer secondary stoichiometries where the ratio of secondary to primary fuel and, hence, the ratio of secondary fuel-nitrogen to primary NO was high. These results indicate that reburning effectiveness is limited by low-NO_x primary burners and by high-nitrogen secondary fuels.

Adiabatic flame temperatures were increased by decreasing the diluent nitrogen flow to the primary. The actual increase in secondary flame temperature was not measured; however, it was probably much less than adiabatic due to heat loss to the reactor wall. An increase in adiabatic flame temperature of about 400^{o}C resulted in an increase in secondary wall temperature of

TABLE 2-2. REBURNING TEST CONDITIONS

Figure	Variable	Temperature		Primary NO (ppm)	Secondary Stoichiometry (percent T.A.)	Secondary (NH_3/CH_4) (Percent)
		Secondary Adiabatic (C)	Secondary Wall (C)			
2-17	Stoichiometry	1400	1270	75	70-115	0, 0.5
2-18	Stoichiometry	1800	1285	115	75-100	0, 0.5
2-19	Primary NO	1800	1270	100-530	90	0, 0.5
2-20	Secondary NH_3	1700	1265	520	90	0.2-1.1
2-21 - 2-24	Stoichiometry	1700	1275	540	75-100	0, 0.5

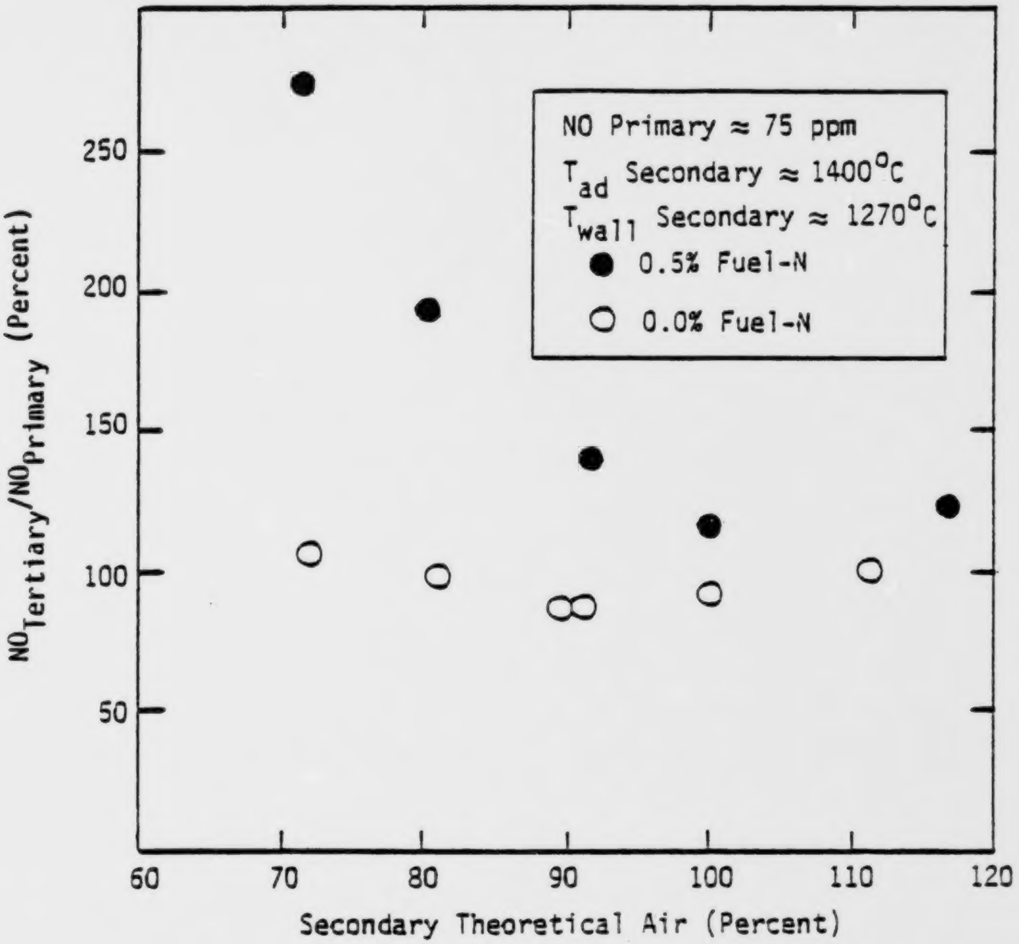


Figure 2-17. Low Temperature, Low NO Primary.

only 13°C as measured by a 0.25-inch (0.64 cm) diameter sheathed thermocouple. Figure 2-18 shows the results of a high-temperature run under conditions otherwise similar to those of Figure 2-17. As in the low-temperature case, the optimum stoichiometry for the fuel-nitrogen-free secondary was around 90 percent theoretical air. Reduction of NO by reburning was slightly improved over the low-temperature case as the tertiary-to-primary NO ratio decreased from 88 to 82 percent. Reburning with a secondary fuel containing 0.5-percent fuel-nitrogen again caused an increase in tertiary NO emissions which became more pronounced at richer secondary stoichiometries, although the increase in NO was less than the corresponding increase in NO at lower temperatures. These results indicate that increased temperature may slightly improve NO removal in the application of reburning to a low-NO_x combustion gas, but even at high temperatures reburning is counterproductive when the secondary fuel has a high fuel-nitrogen content.

The effect of primary NO concentration was investigated by varying the dopant NO flow to the primary. Figure 2-19 shows that at the optimum secondary stoichiometry of 90 percent theoretical air, the fraction of NO removed by reburning with a nitrogen-free secondary fuel increased with increasing primary NO concentration. The fraction of primary NO which was emitted as NO in the tertiary dropped from 82 percent to around 52 percent as primary NO concentration was increased from 115 ppm to about 520 ppm. A similar but sharper decline in the tertiary-to-primary NO ratio was observed when 0.5-percent ammonia was added to the secondary fuel. The ratio decreased from about 115 percent to about 54 percent as the primary NO concentration was increased from 115 ppm to about 520 ppm. For this 120 percent theoretical air primary, 90 percent theoretical air secondary, 120 percent theoretical air tertiary, high-temperature case, for a fuel containing 0.5-percent fuel nitrogen, 115 ppm primary NO corresponded to a primary conversion of about 2.5 percent and 520 ppm primary NO corresponded to a primary conversion of about 11.9 percent. The break-even point where reburning with a 0.5-percent nitrogen-containing fuel neither increased nor decreased NO emissions occurred at a primary NO concentration of around 160 ppm, corresponding to a primary conversion of around 3.5 percent. These results indicate that reburning becomes a more effective method for NO removal as primary NO concen-

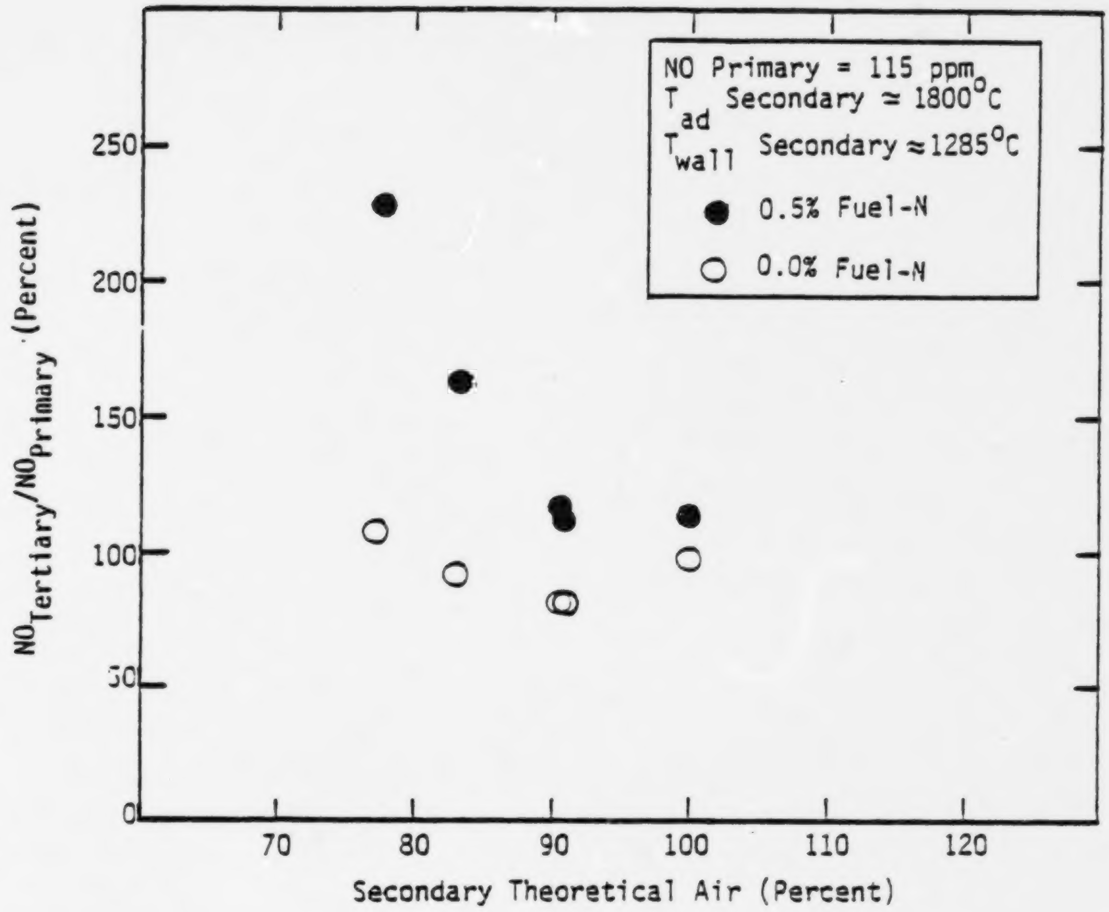


Figure 2-18. High Temperature, Low NO Primary.

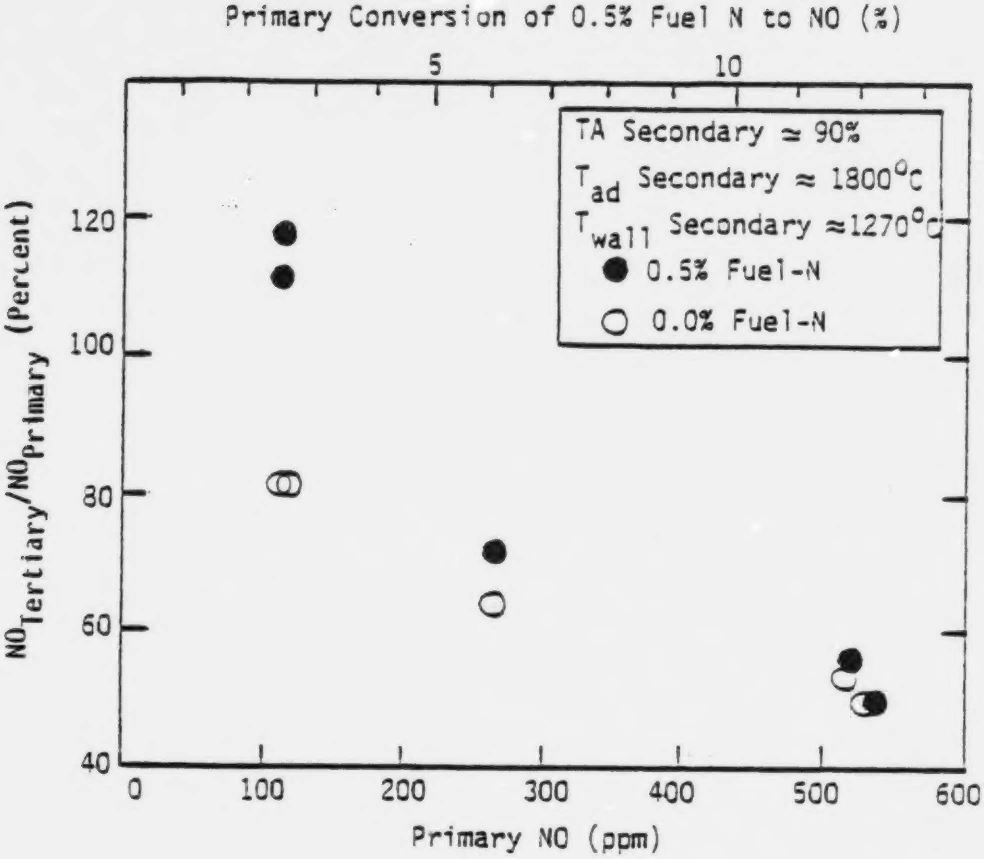


Figure 2-19. Primary NO Concentration Effects.

tration increases, and that presence of fuel nitrogen in the secondary has little effect on NO emissions from a reburned high-NO_x combustion gas.

The influence of fuel-nitrogen content was investigated by varying the proportion of ammonia in the secondary fuel. Figure 2-20 shows that when a high NO_x combustion gas was reburned at a secondary stoichiometry of 90 percent theoretical air, tertiary-to-primary NO ratio increased only slightly with increasing secondary fuel-nitrogen content at NH_3/CH_4 levels of between 0.19 and 1.07 percent, corresponding to secondary NH_3-to-primary NO ratios between 1 and 6. Even for the high-nitrogen fuel, tertiary NO emissions were only marginally increased in the presence of secondary fuel nitrogen. These results indicate that fuel-nitrogen content has less influence than primary NO concentration on the effectiveness of NO removal by reburning.

Figures 2-21 through 2-24 show the effects of secondary stoichiometry when reburning is applied to a high-temperature, high-NO_x combustion gas. Overall reburning effectiveness was examined utilizing the tertiary-to-primary NO ratio, and fixed-nitrogen intermediate formation was investigated by sampling the secondary for NH_3 and HCN. Relative reductions occurring within the secondary and tertiary stages were examined, comparing total fixed-nitrogen levels in the secondary with tertiary NO levels.

Figure 2-21 shows that at the optimum secondary stoichiometry of around 90 percent theoretical air, approximately half of the NO was removed in reburning regardless of whether or not the secondary fuel contained 0.5 percent NH_3. The tertiary-to-primary NO ratio at richer secondary stoichiometries increased more rapidly when fuel nitrogen was present in the secondary due to the increased ratio of secondary-to-primary fuel. Figure 2-22 shows fixed nitrogen (XN) levels in the secondary under the same conditions. The open data points and solid lines indicate the absence of fuel nitrogen in the secondary, and the shaded points and dashed lines indicate the presence of 0.5 percent ammonia in the secondary fuel. Circles denote NO, triangles HCN, and squares represent NH_3. Secondary NO levels did not appear to be influenced by the presence of fuel nitrogen in the secondary; however, NO dropped sharply as secondary stoichiometry became richer. This drop in NO was offset by a corresponding rise in HCN, the dominant fixed-nitrogen species at rich secondary stoichiometries. Secondary HCN levels were about

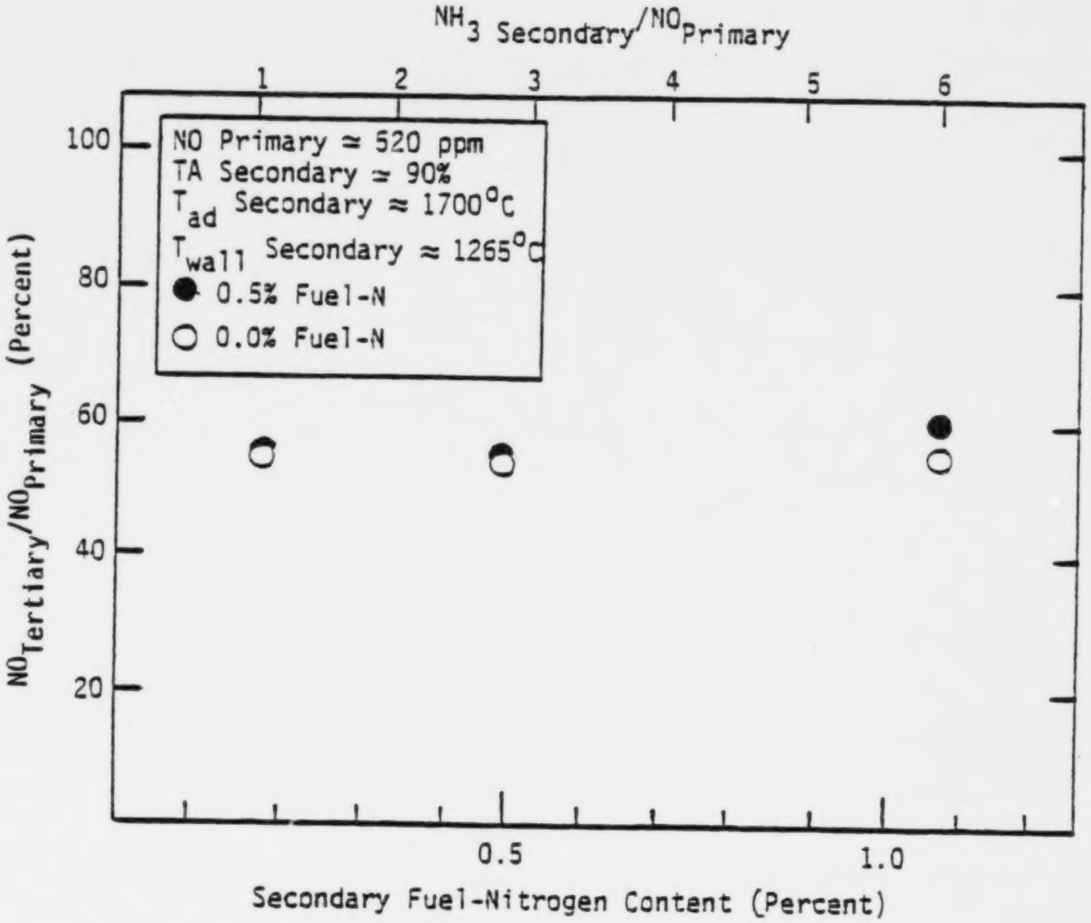


Figure 2-20. High NO Primary, Secondary Fuel Nitrogen Effects.

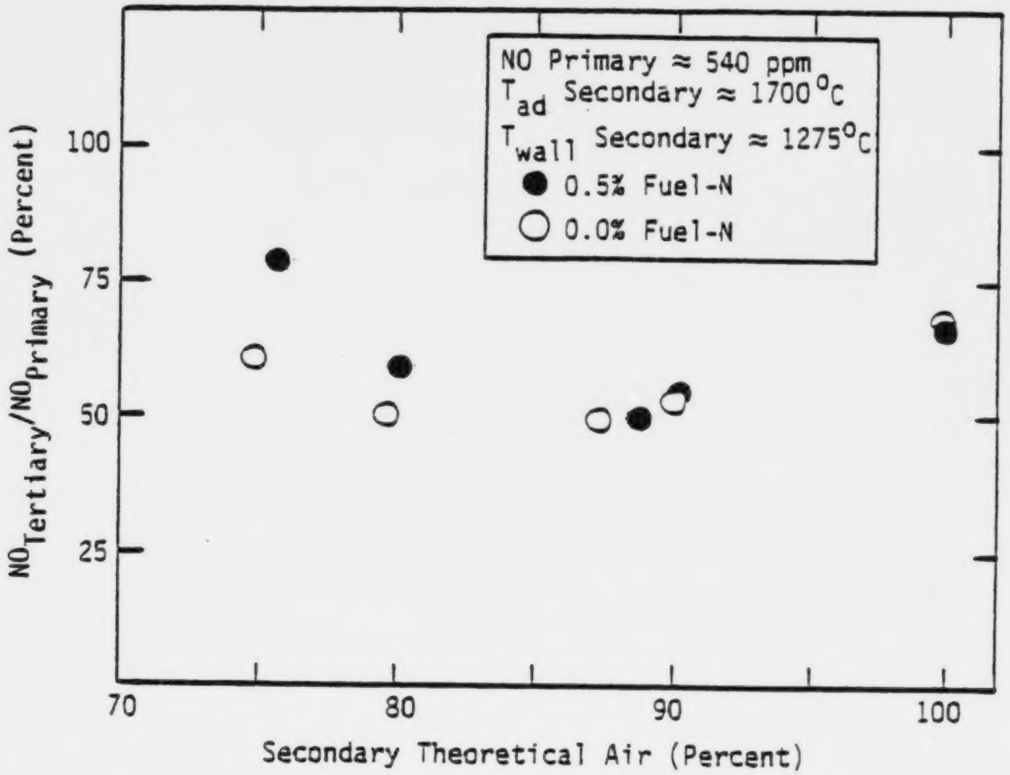


Figure 2-21. High Temperature, High NO Primary.

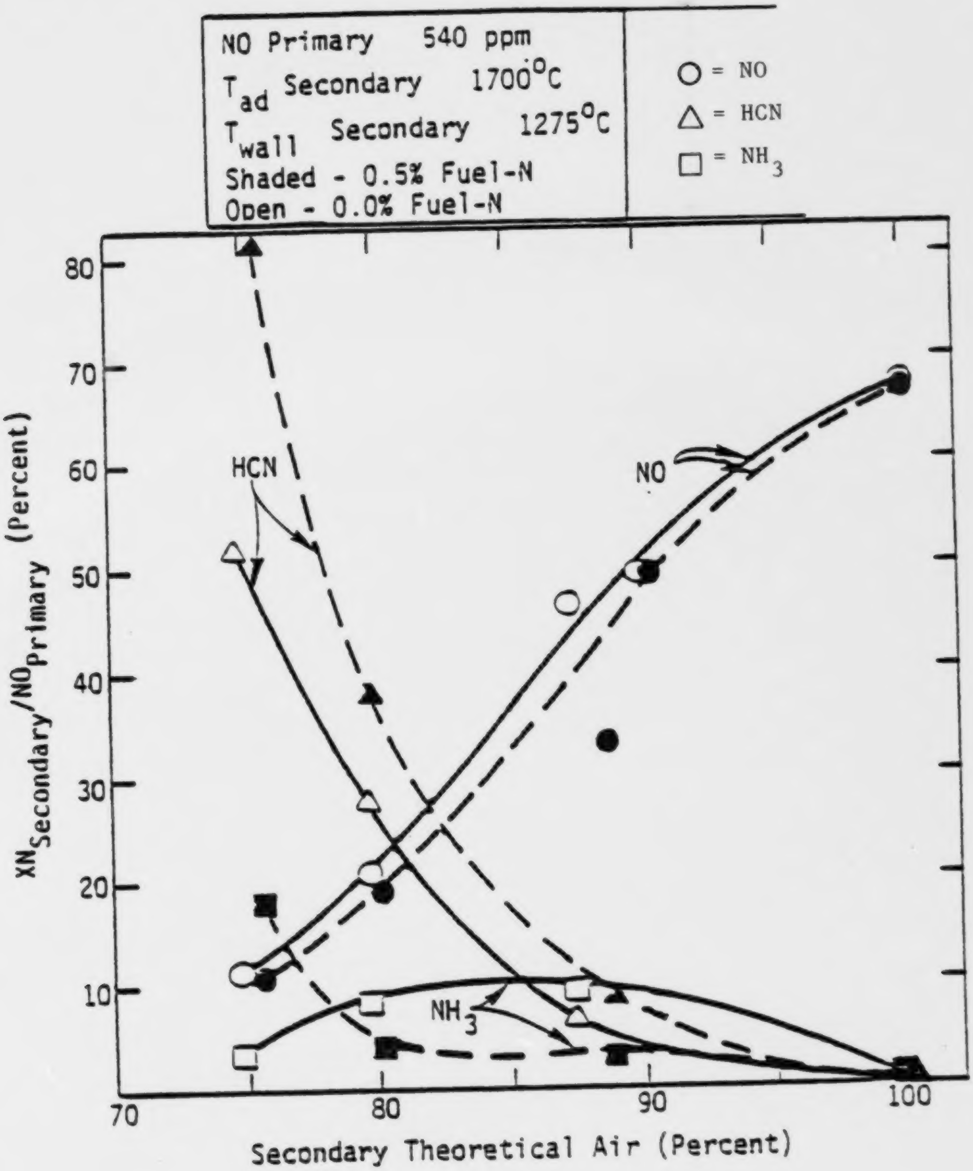


Figure 2-22. Secondary XN.

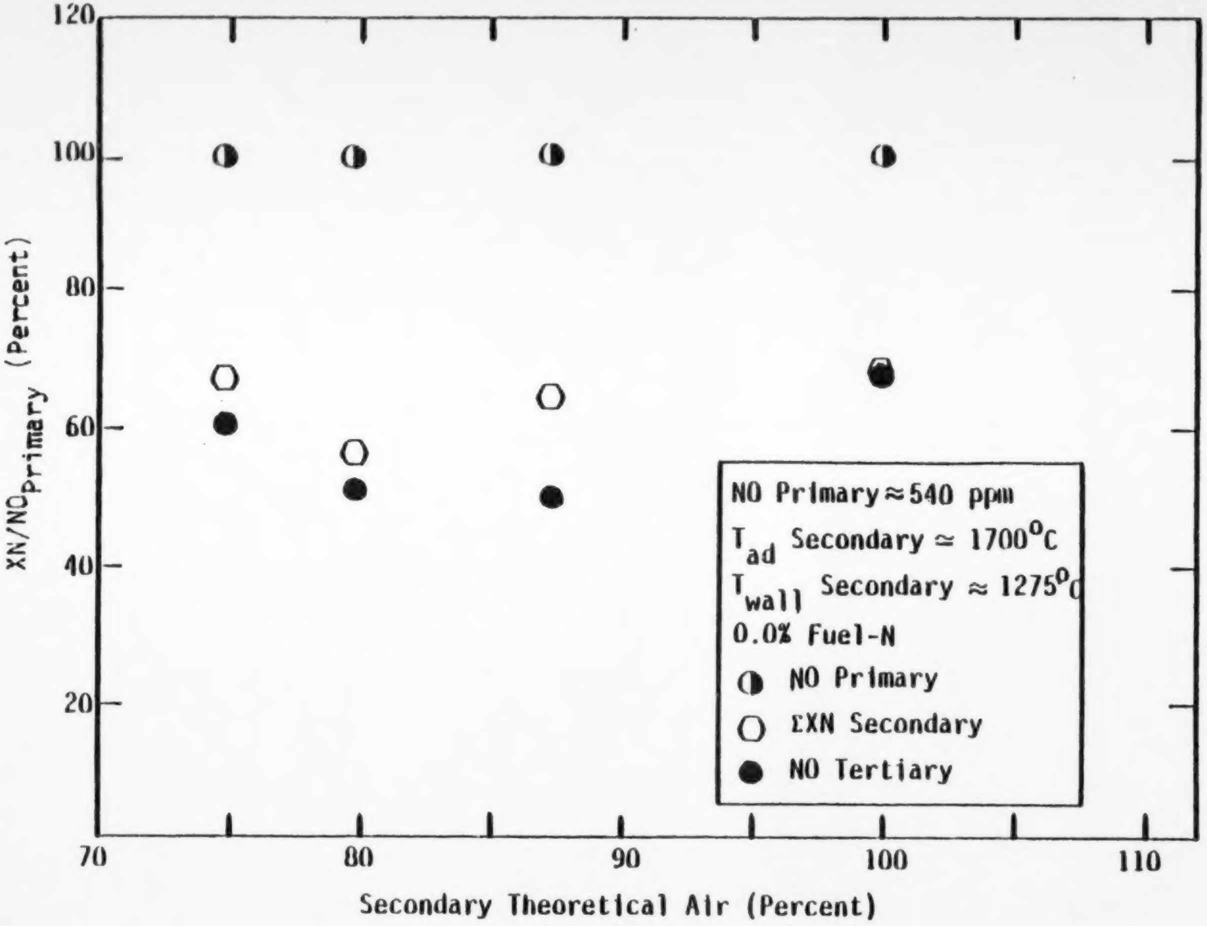


Figure 2-23. Fuel Nitrogen-Free Secondary, Comparison of Stages.

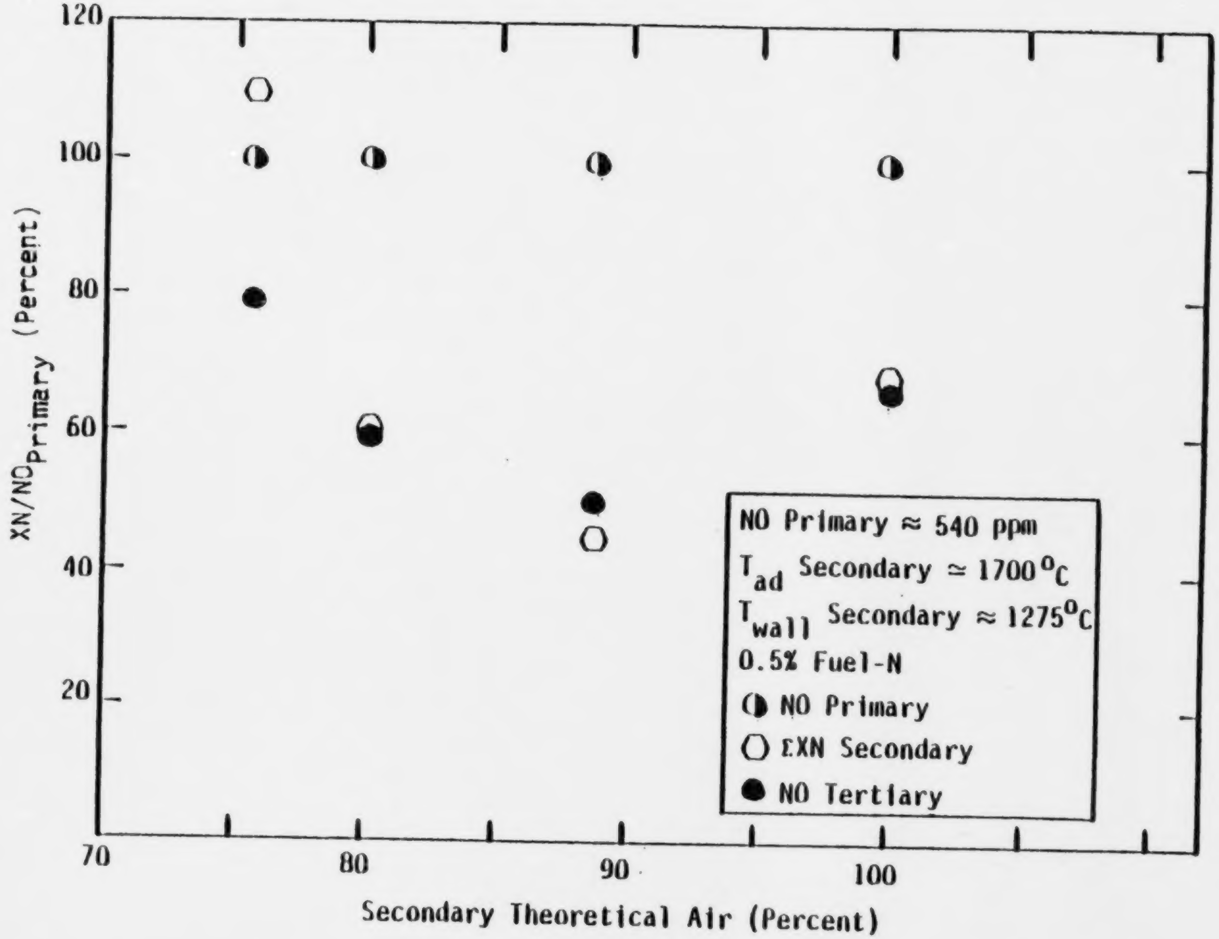


Figure 2-24. Fuel Nitrogen in Secondary, Comparison of Stages.

50 percent higher when fuel nitrogen was included in the secondary. The ammonia measurements yielded the most interesting results. In the absence of secondary fuel nitrogen, NH_3 peaked at about 10 percent of the primary NO level at a secondary stoichiometry around 90 percent theoretical air, the optimum stoichiometry for NO removal in reburning, and decreased as the secondary became richer. When the secondary fuel contained 0.5-percent nitrogen in the form of ammonia, secondary NH_3 levels increased slowly as the secondary stoichiometry became richer, remaining well below NH_3 levels measured in the absence of secondary fuel nitrogen. At very rich secondary stoichiometries, however, NH_3 rose sharply in the fuel-nitrogen-containing secondary. These results suggest that an optimum secondary stoichiometry exists for NO removal by reburning. At richer secondary stoichiometries, HCN becomes the dominant fixed-nitrogen species in the secondary and is easily reoxidized to form NO in the tertiary. Presence of fuel nitrogen in the secondary contributes to HCN formation sharpening the optimum secondary stoichiometry.

Figures 2-23 and 2-24 show the relative fixed nitrogen levels in each of the three stages. The half-shaded points represent primary NO, always 100 percent because primary NO is used as the base for comparison; the open hexagons are total fixed nitrogen (ΣXN) in the secondary where the three measured fixed nitrogen species are NO, HCN, and NH_3; and the shaded points are tertiary NO. Occasional NO_2 measurements (NO_x-NO) were taken in the tertiary and in the primary; these were always negligible. When fuel nitrogen was not included in the secondary, as shown in Figure 2-23, the difference between primary NO and secondary ΣXN was greater than the difference between secondary ΣXN and tertiary NO, indicating that most of the reduction in fixed-nitrogen occurred in the secondary. It is interesting to note that the minimum in secondary ΣXN occurred at 80 percent theoretical air secondary, whereas the minimum in tertiary NO occurred at a leaner secondary stoichiometry corresponding to the peak in secondary NH_3 (Figure 2-22). This suggests that secondary NH_3 formation may contribute to NO reduction by thermal deNO_x reactions in the tertiary (Lyon, 1975). Figure 2-24 shows that when fuel nitrogen was included in the secondary, essentially all of the NO reduction occurred in the secondary stage at all but the richest secondary stoichiometry. In fact, at a secondary stoichiometry around 90 percent theoretical air, tertiary NO was slightly greater than secondary ΣXN possibly due to thermal NO_x formation in the tertiary. These results indicate that under the high-temperature, high-primary NO_x conditions investigated, most of the fixed-nitrogen reduction in reburning occurs in the secondary stage; however, the tertiary stage becomes important if significant NH_3 formation occurs in the secondary.

3.0 ANALYSIS OF THE REBURNING PROCESS

The following material describes the use of the FCR kinetic mechanism to simulate reburning. The presentation is organized into a brief description of the kinetic mechanism and a description of the results of specific calculations.

The purpose of the FCR mechanism is to model the gas phase kinetics of the combustion of hydrocarbons of structure C_2 or simpler, including fuel nitrogen processing. The methodology that was adopted for the development of the FCR mechanism tested each portion of the kinetic separately before coupling into the overall mechanism. The individual portions which make up the network are:

- H_2/O_2
- $CO/H_2/O_2$
- NH_3
- HCN
- CH_4/C_2

The mechanism was verified by comparing the results of direct simulations of well characterized experimental data with the original data. These comparisons were only performed using the necessary reactions (i.e., modeling data on H_2/O_2 combustion requires only the H_2/O_2 reactions). This approach permitted the verification process to proceed from simple to complex kinetic sets and to examine each portion of the mechanism in the most critical manner possible.

Limitations on Nitrogen Chemistry

Since the present calculations are strongly dependent on the nitrogen chemistry, it is appropriate to list *a priori* the limitation on the current set.

Two problem areas have been noted in the use of the ammonia set: reactions of NH_i compounds to yield N_2H_i species, and the reaction $NH_2 + NO$. The reactions of NH_i species together occur only in high amine loading situations, which is of no concern under conditions of interest for reburning. However, the reaction of NH_2 with NO is indicated to be a prominant pathway for fixed nitrogen reduction in most modeled systems. The reaction sequence which represents the overall effect is complex, and at present can only be approximated with non-elementary reactions. An example which can be used to represent the overall reaction pathway are:

$$NH_2 + NO \rightarrow N_2 + H_2O$$

$$NH_2 + NO \rightarrow N_2 + H + OH$$

Rate studies indicate two temperature regimes: low temperature with a weak temperature dependence, and high temperature with a strong temperature dependence. The crossover is indicated to be 1900 K. In light of the importance of this reaction to fixed nitrogen reduction, satisfactory predictions cannot be expected for all cases until it is represented in terms of elementary reactions.

Insufficient elementary rate data are available to complete characterize the HCN system. This is particularly true of the rates involving nitrogen-hydrocarbon fragment interactions. Most of these rates are either original estimates, or estimates due to others. Elementary rate data which are available are frequently obtained at low temperatures. Although the HCN set has performed adequately in many simulations, discrepancies still exist. Specific discussion of these limitations will be presented with the discussion of results.

Process Description

The objective in performing these calculations was to gain an understanding of the reburn process in terms of elementary kinetics, and to explore the effects of parameters on the limits of process performance.

The reburn process was modeled by the configuration shown in Figure 3-1. The stirred reactor (SR) simulates the fuel-lean primary zone. The effluent is mixed with the reburn methane over 25 msec and is allowed to burn out for 300 msec. Conditions for the SR, which was always held at 1844 K, are shown in the figure. Conditions in the secondary zone were varied by changing reburn fuel flow, plug flow temperature, and plug flow residence time. Conditions examined are shown below:

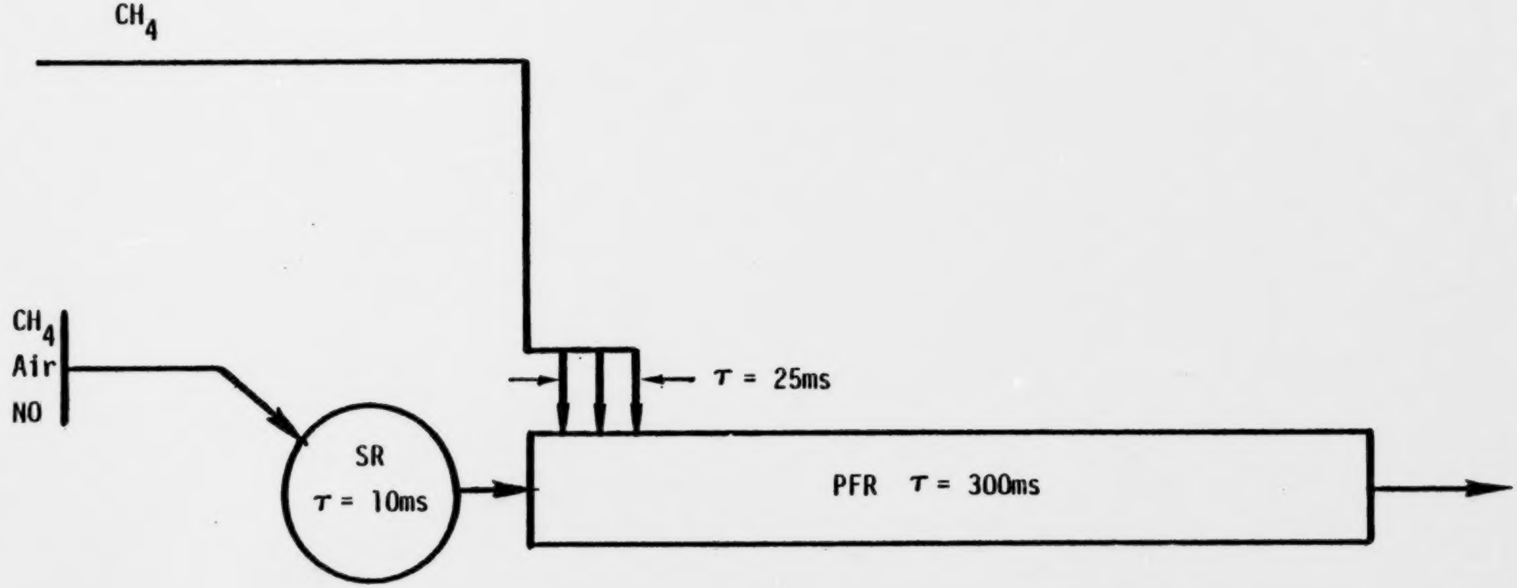
- Temperature: 1844, 1700, 1600, 1500, 1400 K.
- Stoichiometry: 4.00, 2.50, 1.68, 1.00, 5.0 (values are equivalence ratio based on secondary fuel and primary O_2).
- Residence Time: 0, 25, 50, 100, 300 msec.
- Mixing Time for Secondary Fuel: 0, 25 msec.

These parameters were selected to cover the range of experimental studies, bridge the gaps between these studies, and to explore beyond the data.

The results for temperature and stoichiometry variations are shown in Figure 3-2 as percent unremoved NO at the plug flow reactor (PFR) exit. Important features include:

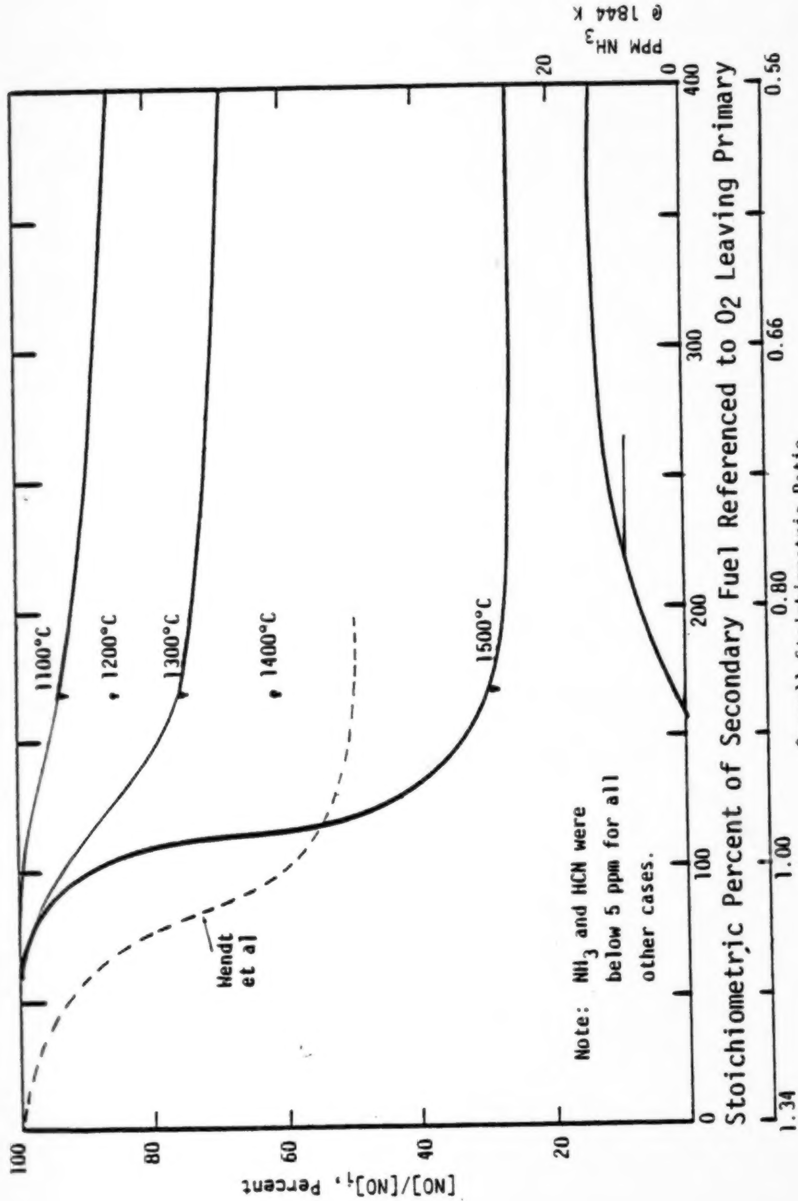
- Increasing NO reduction with temperature.
- Small dependence on stoichiometry for secondary fuel flows when overall stoichiometry was fuel-rich.
- NO reduction was strongly dependent on stoichiometry near the stoichiometric point.
- NH_3 tended to increase with increasing PFR time. The plotted case shows the maximum NH_3 predicted.
- HCN (not shown) decreases throughout the PFR, is favored by higher temperatures and fuel-rich conditions, and never exceeds 4 ppm.

The effect of residence time is shown in Figure 3-3 for the stoichiometry -temperature values. The majority of the NO reduction occurs in the same


CH_4
CH_4
Air
NO
SR
τ = 10ms
τ = 25ms
PFR τ = 300ms

SR: ϕ = 0.74
O_2 = 5%
NO = 517 ppm
τ = 1844 K

Figure 3-1. Configuration for the Reburn Model.



Note: NH_3 and HCN were below 5 ppm for all other cases.

Figure 3-2. Reduction of NO as a Function of Stoichiometry.

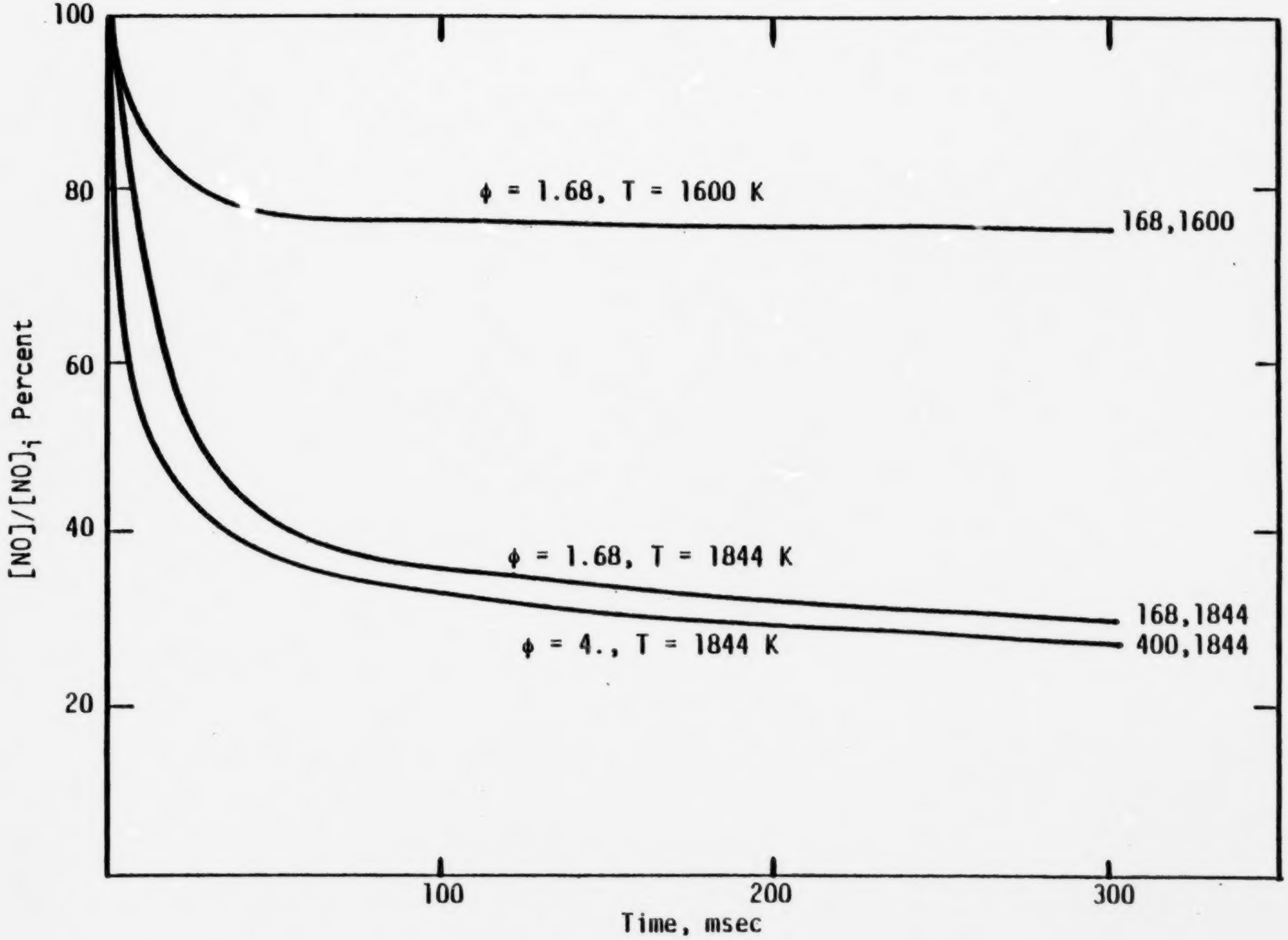


Figure 3-3. Reduction of NO as a Function of Time.

first 25 msec over which the fuel is added. No difference was seen between adding the fuel instantly and spacing the addition over 25 msec.

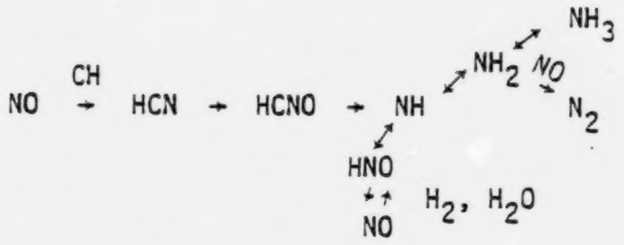
Analysis of the mechanism showed the following pathway was responsible for NO removal:

$$NO + CH \rightarrow CHO + N \qquad (1)$$

$$N + NO \rightarrow N_2 + O \qquad (2)$$

$$N + O_2 \rightarrow NO + O \qquad (3)$$

The radical CH actually increases with decreasing richness for fuel-rich conditions. This is because O_2 favors the breakdown of CH_4 into hydrocarbon fragments. However, increasing O_2 cancels the effect of more CH as conditions become leaner. Reactions (1) and (3) combine to hold N-atom constant at fuel-rich conditions, which accounts for the near independence of NO reduction. As a stoichiometric mixture is approached, O_2 rises dramatically and CH is reduced, which prevents NO reduction. Other pathways are involved, the prime example being:



Two points must be made regarding these calculations. First, the uncertainty in kinetic rates, particularly regarding radical reactions in the CH and HCN systems, prevents quantitative simulation. Compared to the experimental data presented here and the Japanese data, the simulated data show too little reduction in NO at low temperatures. However, the data trends are well predicted, which indicates that the controlling processes are correctly modeled even if absolute rate coefficients are not accurate. The second concern involves the identity of the hydrocarbon radical attacking NO. In the work of both Myerson (1975) and Shaub and Bauer (1978), the rapid attack of a hydrocarbon fragment on NO was indicated. Both authors suspect CH to be the reacting species. Indeed, Shaub and Bauer (1978) present a convincing argument. However, direct evidence is still lacking. Alternate reactions involving CH_2 are possible.

The following conclusions have been drawn from the modeling work:

- Reduction of NO by reburning appears to be caused by hydrocarbon attack on NO, following which the released N-atom combined into N by the reverse Zeldovich step.
- NO reduction is favored by higher temperatures, probably to the limit where direct attack of hydrocarbon fragments on N_2 become important.
- At fuel-rich conditions NO reduction appears to be relatively independent of stoichiometry. This is due to a balancing of NO reduction by CH with NO formation by N + O_2.

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Myerson, A.L., Fifteenth Symposium (International) on Combustion, The Combustion Institute, pp. 1085 (1975).

Shaub, W.M., and S.H. Bauer, Combustion and Flame 32, 35 (1978).

Takahashi, Y., et al., "Development of Mitsubishi 'MACT,' In-Furnace NO_x Removal Process," presented at U.S.-Japan NO_x Information Exchange, Tokyo, Japan, May 1981.

Wendt, J.O.L., C.V. Sternling, and M.A. Matovich, Fourteenth Symposium (International) on Combustion, The Combustion Institute, pp. 897 (1973).

APPENDIX B

BENCH-SCALE STUDIES ON THE EFFECTIVENESS OF REBURNING FOR IN-FURNACE NO_x REMOVAL

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An EPA Fundamental Combustion Research
Project Report

June, 1982

1.0 INTRODUCTION

In the past ten years there have been considerable advances in the use of combustion modification to control the emission of nitrogen oxides (NO_x) from coal-fired power plants. Although NO_x emissions can be reduced by low excess air-firing and removing burner out-of-service (BOOS) to create a fuel-rich zone, the most significant reductions have been achieved by redesigning the firing systems. Low NO_x burners reduce emissions up to 75 percent of those produced with conventional high-turbulent burners(1, 2). Further reductions are possible if low NO_x burners are fitted with overfire air ports. Tangential-fired boilers tend to be inherently low producers of nitrogen oxides. Emissions can be reduced still further and currently a concept referred to as "Low NO_x Concentric Firing" (LNCF) is being evaluated by the EPA(3). Other low NO_x boiler concepts are based upon pilot-scale studies with a coal-fired pre-chamber(2) and have the potential to reduce emissions to less than 150 ppm. This report is concerned with a control concept which can further reduce emissions from a low NO_x firing system by reburning.

The MACT (Mitsubishi Advanced Combustion Technology) in-furnace NO_x removal process applies the concept of reburning to a boiler. Part of the fuel bypasses the main heat-release zone and is injected above the main burners to provide the fuel for reburning. It is claimed that the NO_x produced by the main firing system can be reduced "to half at any level of concentration". In an in-furnace de-NO_x combustion test using a low NO_x gas burner, NO_x emissions as low as 8 ppm (calculated at 5 percent oxygen) have been reported(4). Other data indicate that irrespective of the fuel used, the NO_x level in the main burner is lowered by about 50 percent.

The basic concepts associated with in-furnace NO_x reduction by reburning are not new. The reduction of NO by flames has been appreciated for over a decade. A flue gas NO_x incinerator was developed by the John Zinc Company(5). The term 'reburning' was coined by Wendt, Sternling and Matovich(6) who reduced NO produced in a laboratory-scale flat-flame by adding methane or ammonia to the combustion products. In-furnace NO_x reduction can be divided into two processes (see Figure 1): NO reduction and TFN conversion. In the NO reduction zone the reburning fuel mixes with the products from the main burner zone. With coal as the reburning fuel, devolatilization occurs producing char and a mixture of hydrocarbon volatiles containing bound nitrogen. Three major general reactions take place in the NO reduction zone which affect the reburning process:

1. NO reacts with hydrocarbon radicals by reactions such as

   $$\begin{aligned} NO + CH &\rightarrow N + CHO \\ &\rightarrow HCN + O \end{aligned}$$

   which increases the nitrogen radical pool.

2. Interconversion of nitrogen species among different fixed nitrogen compounds (TFN = $NO + HCN + NH_3$).

3. The formation of molecular nitrogen by the reaction of nitrogen radicals with NO. The reaction

   $$NO + N \rightarrow N_2 + O$$

   is the most probable path although reactions with NH_i species are possible.

Consequently, the exhaust from the NO reduction zone will contain fixed nitrogen compounds, but their sum may be less than the equivalent NO produced by the main burner zone.

The second process associated with in-furnace NO_x reduction is the addition of air to burn out the partially-oxidized products formed in the NO reduction zone which also results in the conversion of TFN to NO. Emissions are minimized if the TFN conversion is minimized and this zone is analogous to the second stage of a staged combustion process. Combustion must be completed efficiently, but the ultimate NO level must be minimized.

This report describes data obtained in bench-scale investigations with pulverized coal to establish the parameters which control the effectiveness of reburning. The work was conducted as part of the EPA Fundamental Combustion

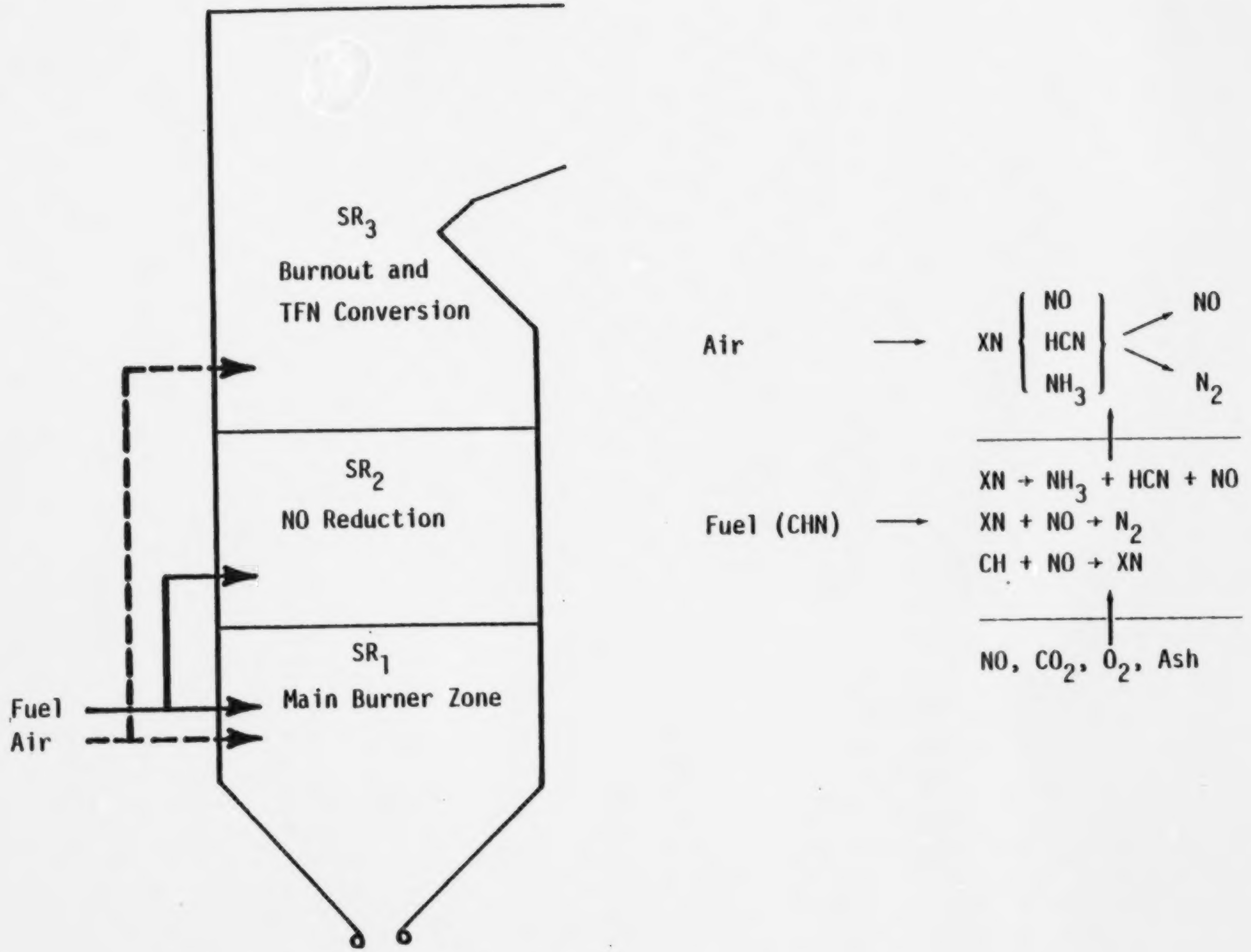
SR$_3$
Burnout and
TFN Conversion
SR$_2$
NO Reduction
SR$_1$
Main Burner Zone
Fuel
Air
Air
XN
NO
HCN
NH$_3$
NO
N$_2$
XN → NH$_3$ + HCN + NO
Fuel (CHN)
XN + NO → N$_2$
CH + NO → XN
NO, CO$_2$, O$_2$, Ash

Figure 1. The In-Furnace NO_x Reduction Process.

Research Program. The basic guidance for the study was provided by the earlier research of Kramlich, Clark, and Seeker (included here as Appendix A). The bench-scale studies gave an indication of the impact of heterogeneous processes and the potential problems that could occur with pulverized coal as the reburning fuel.

2.0 EXPERIMENTAL SYSTEMS

The experimental investigations in this study were carried out in the bench-scale furnace shown in Figure 2. This is a refractory lined reactor which consists of five separate sections, has a 15.2 cm internal diameter, and is 1.2 meters long. The furnace entry (top section) includes a 30.5 cm long refractory quarl that gradually diverges from 5.1 cm to the full 15.2 cm diameter. The long quarl helps to eliminate recirculation and improves the one-dimensionality of the flow field. The primary stage could be fired either with pulverized coal/air or propane/air doped with NO to control the level of NO at the primary zone exit. All of the coal experiments were conducted with the premixed burner. A removable radiation shield was used to isolate the primary zone from the rest of the furnace.

The reburning fuel (either Utah or a Beulah pulverized coal) was injected downstream of the radiation shield through an axial fuel injector. Nitrogen was used to transport the pulverized coal in all experiments. A removable staging choke separated the NO reduction zone from the burnout zone. Air to complete the combustion was supplied through a radial injection ring positioned after the staging choke. Side ports allowed the insertion of removable cooling coils in both the secondary and tertiary zones.

Exhaust samples were withdrawn from the reactor stack with a stainless steel, water-jacketed probe and analyzed using continuous instrumentation (chemiluminescent NO, paramagnetic O_2, and NDIR CO and CO_2). A water-spray probe was used for extracting in-flame samples. Gas-phase HCN and NH_3 samples were collected in a gas washing unit which consisted of an impinger in series with a bubbler containing a fritted glass cylinder. The sample solutions were subsequently analyzed for CN^- and dissolved NH_3 using specific ion electrodes. A solution of lead carbonate and sodium carbonate was used in the impinger and the bubbler to remove sulfite ions. The probe and analysis systems were validated by sampling gases of known composition.

Table 1 shows a complete analysis of the Utah and Beulah coals used in this study. The Utah coal is a high-volatile B bituminous fuel which contains approximately 1.5 percent nitrogen. The Beulah coal is a lignite from North Dakota which contains approximately 0.96 percent nitrogen.

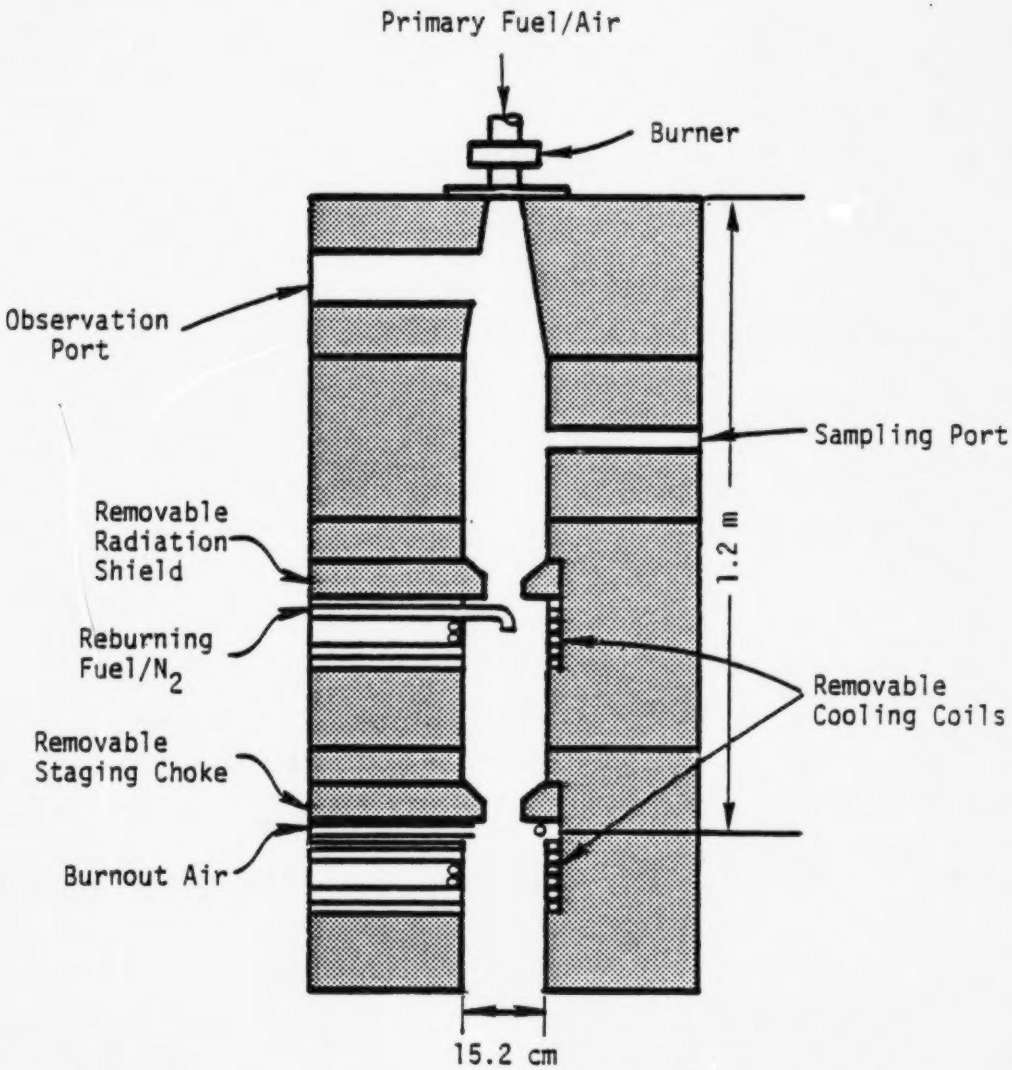
Primary Fuel/Air
Burner
Observation Port
Sampling Port
1.2 m
Removable Radiation Shield
Reburning Fuel/N2
Removable Cooling Coils
Removable Staging Choke
Burnout Air
15.2 cm

Figure 2. Bench Scale Coal Fired System.

TABLE 1. COAL PROPERTIES

	UTAH	BEULAH
Proximate Analysis (As Received)		
Moisture	6.39	34.63
Ash	7.40	4.97
Volatile Matter	38.89	27.02
Fixed Carbon	47.32	33.38
Ultimate Analysis (% Dry)		
Carbon	73.17	66.15
Hydrogen	5.55	4.20
Nitrogen	1.54	.96
Sulfur	.66	.37
Ash	7.90	7.60
Oxygen	11.18	20.72
Rank	HVB Bituminous	Lignite A

3.0 PROPANE/COAL RESULTS

This section of the report discusses the results which were obtained with propane as the primary zone fuel. The NO level at the exit of the primary zone was controlled by adding pure NO to the inlet propane/air stream. The primary zone NO levels are reported on a ppm (volume) basis reduced to 0 percent O_2. The levels were chosen to approximately simulate the primary zone NO concentrations produced when the Beulah and Utah coals were present as the primary zone fuel. All of the experiments were conducted with a primary zone firing rate of 50,000 Btu/hr. Both the primary zone firing rate and the molar NO input rate were maintained constant as the stoichiometry distribution was varied.

The North Dakota lignite (Beulah) and the Utah high-volatile bituminous coal were used as the secondary (reburning) fuel in all of these experiments. The stoichiometry in the secondary zone was varied by altering the pulverized coal firing rate. In this way it was possible to alter the secondary zone conditions without influencing the primary zone conditions. However, this procedure does not allow the total fuel input to be maintained constant.

3.1 Stoichiometry Distribution

The stoichiometry distribution throughout the reactor system was considered in detail. Experiments were conducted to isolate the influence of primary, secondary and teriary stoichiometry. Since the secondary (reburning) zone stoichiometry is most critical, it will be discussed first.

3.1.1 Secondary Zone Stoichiometry (SR_2)

Figure 3 shows typical results on the influence of secondary zone stoichiometry. In these experiments the main fuel was propane doped with NO to 633 ppm (in the primary zone exhaust) and the reburning fuel was the Beulah lignite. The data are reported in terms of the ratio of NO in the furnace exhaust to NO at the exit of the primary zone in percent. (100 percent implies that the concentration in the furnace exhaust is identical to that at the exit of the primary zone without reburning.) Both the primary zone stoichiometry and the tertiary stoichiometry were maintained at 1.1 and 1.25 respectively.

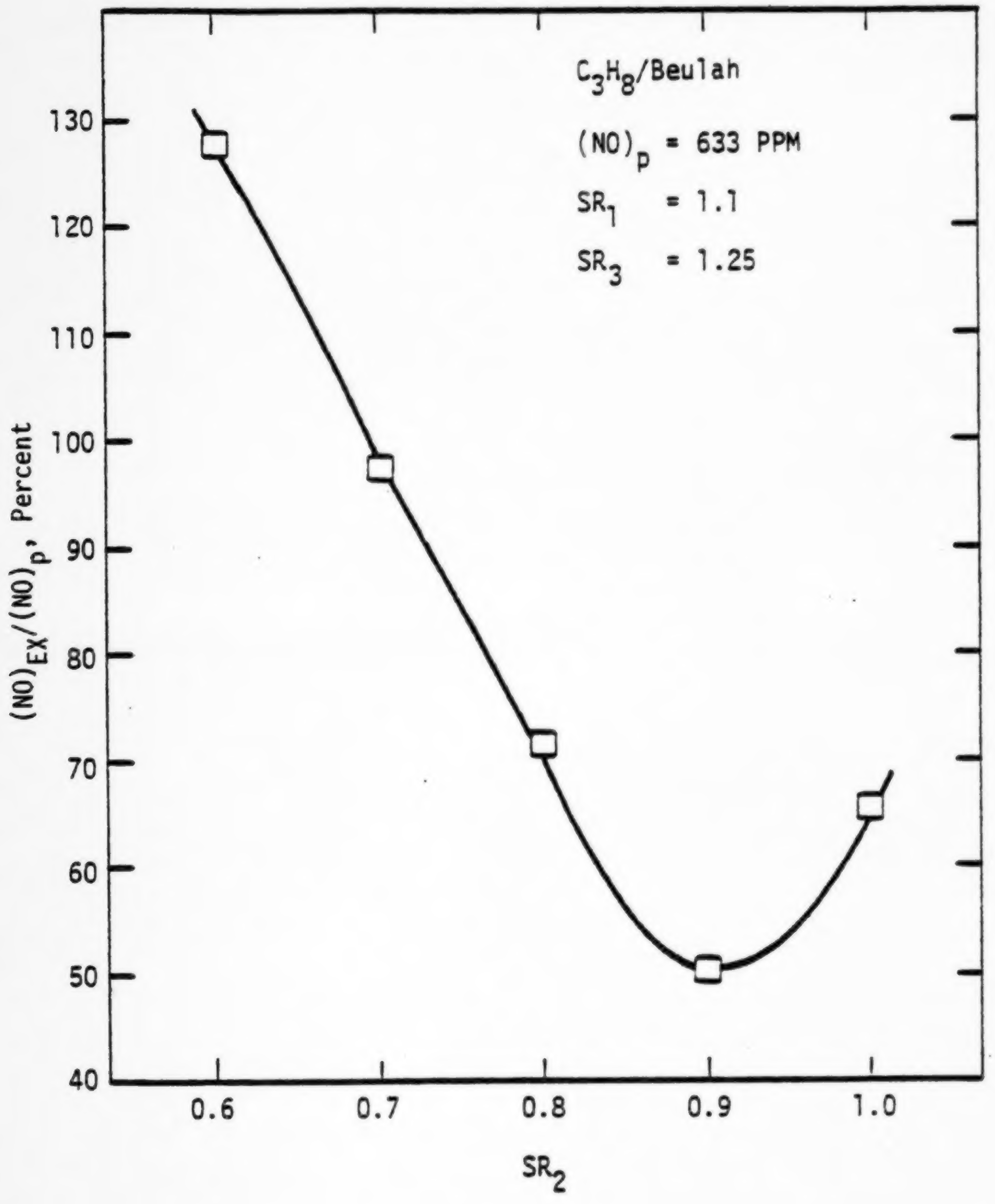

Figure 3. Typical Results on the Influence of SR_2.

The data shown in Figure 3 indicate that as the secondary stoichiometry is reduced below 1.0, significant reductions in NO emissions were achieved. At a secondary zone stoichiometry of 0.9 the exhaust emissions were exactly 50 percent of the emissions without reburning and this is in good agreement with the Japanese results reported previously (4). However, as the reburning stage stoichiometry is further reduced, the exhaust emissions begin to increase. In fact, by $SR_2 = 0.6$, the emissions are above those with no reburning fuel.

As the secondary zone stoichiometry is reduced, the amount of reburning fuel required increases. If the reburning fuel is heavy oil or coal, and contains significant fuel nitrogen, then the reactive nitrogen content of the rich-zone also increases. To investigate the importance of this effect, the data shown in Figure 3 were replotted in terms of percentage conversion of the total reactive nitrogen (primary zone NO + nitrogen added with the coal) to NO in the exhaust. Figure 4 shows these results as a function of secondary zone stoichiometry and indicates that once the reburning zone is rich (SR_2 less than 0.9), the stoichiometry has little effect on the percentage conversion of the available reactive nitrogen.

Figure 5 shows the results of gas-phase concentration measurements made at the end of the secondary zone (fuel-rich). The reader should remember that the purpose of this first reburning zone is to react NO with hydrocarbon radicals by reactions such as:

$NO + CH \rightarrow N + CHO$ and

$NO + CH \rightarrow HCN + O$

Figure 5 indicates that this type of reduction is occurring at all rich-zone stoichiometries as expected. In addition, there appears to be considerable inter-conversion of nitrogen among the different fixed-nitrogen species (XN). As in normal staged combustion, below a rich-zone stoichiometry of approximately 0.8, NH_3 and HCN formation becomes significant. Further, the data in Figure 5 demonstrate that as the secondary zone stoichiometry is reduced, the summation of the XN species increases dramatically. Figure 6 shows these same data replotted; each of the XN species concentrations has been normalized with respect

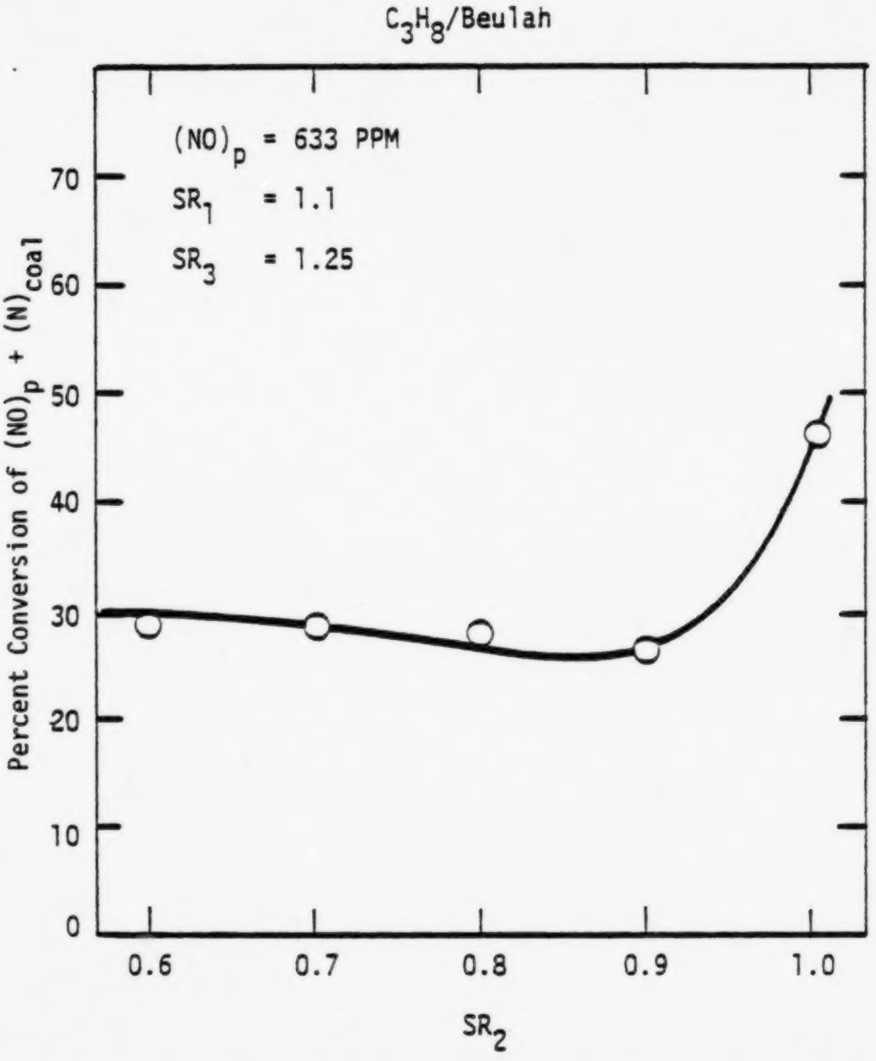

Figure 4. Overall Conversion of Available Nitrogen to Exhaust NO.

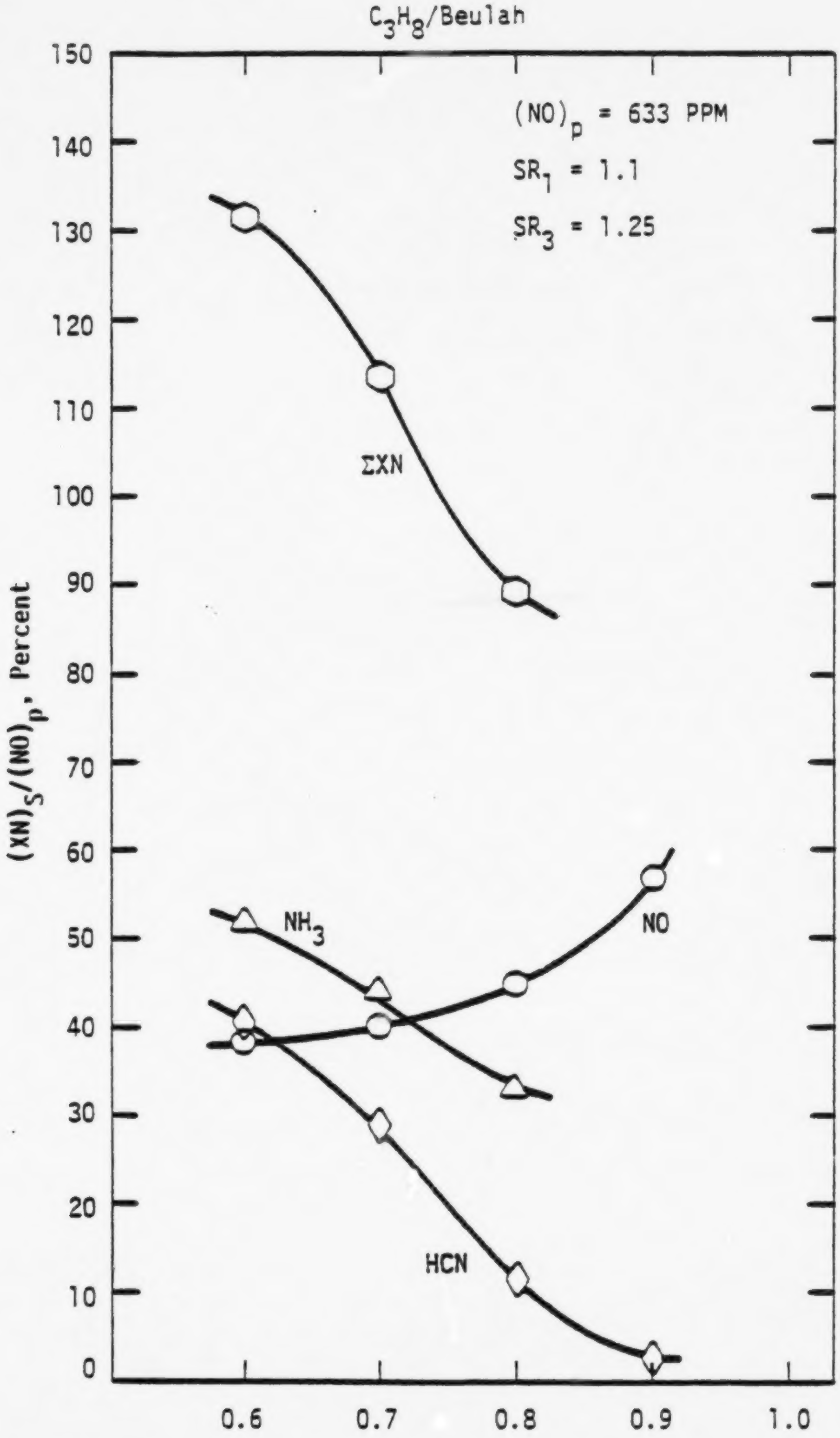

Figure 5. Gas Phase Species Concentration at the Second-Stage Exit.

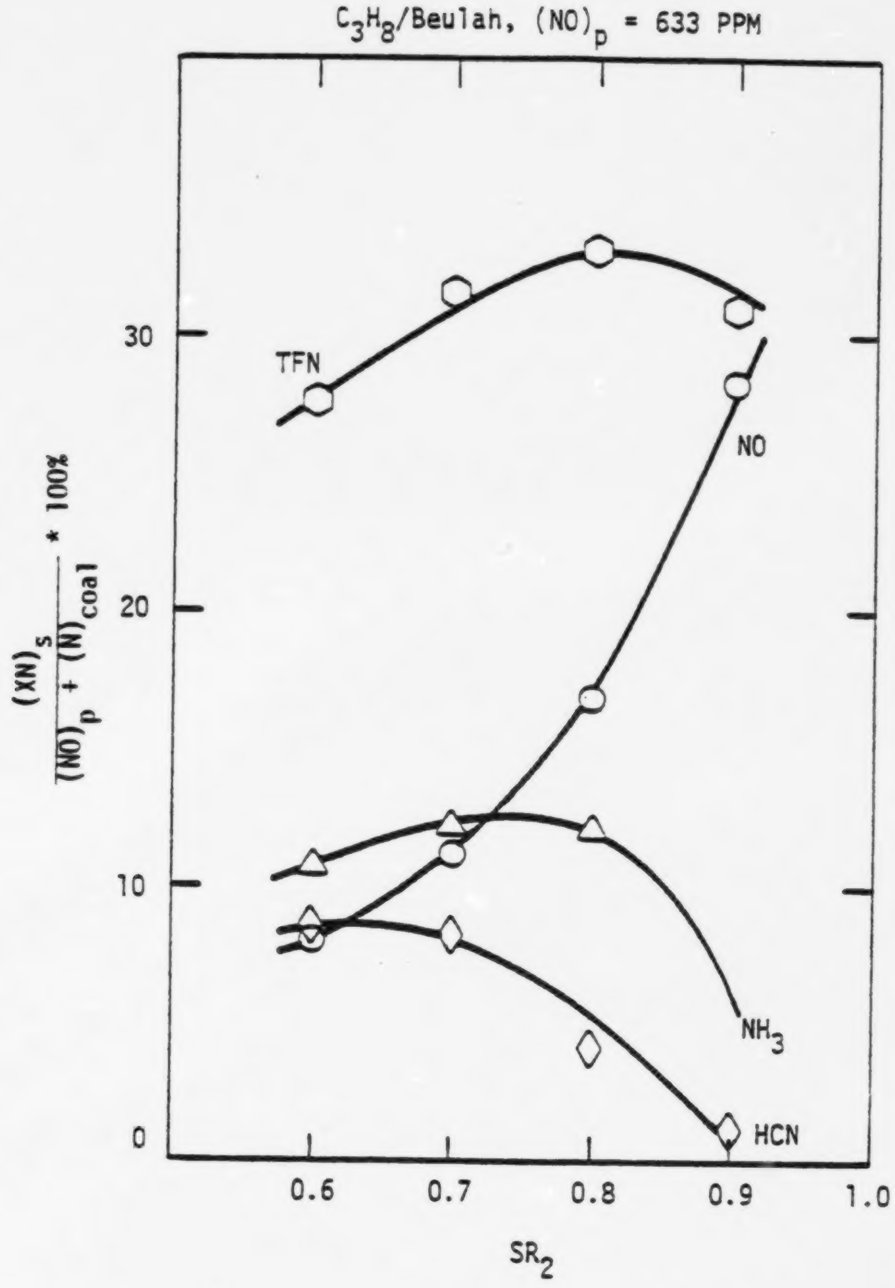

Figure 6. Normalized Species Concentrations at the First-Stage Exit.

to the total available reactive nitrogen in the rich-zone (the NO exiting the primary zone plus the nitrogen in the coal). Figure 6 demonstrates that although the NO exiting the secondary zone decreases dramatically as SR_2 is reduced, the TFN remains approximately 30 percent of the total available nitrogen. Therefore, decreasing the secondary stoichiometry (by adding more reburning fuel) results in higher exhaust NO_x simply because it increases the available reactive nitrogen.

Figure 7 summarizes the fate of the available nitrogen on a cumulative basis and includes consideration of the char nitrogen. (Char nitrogen was estimated based on measured CO and CO_2 concentrations and the assumption that carbon and nitrogen are evolved at approximately the same rate.) These results emphasize that at low secondary zone stoichiometries, char nitrogen can be extremely significant.

Figure 8 summarizes all of the results on the influence of SR_2 by comparing the total XN species (TXN = NO + HCN + NH_3 + char nitrogen) exiting the second stage relative to the NO in the exhaust. Note the greatly expanded ordinate scale . These data clearly demonstrate that a 50 percent reduction in NO emission can be achieved by the addition of an appropriate amount of reburning fuel (in this case to give an SR_2 of 0.9). However, if additional reburning fuel is added to further reduce the second stage stoichiometry, the effectiveness of the reburning concept is decreased. This is a direct result of the increased amount of reactive nitrogen which is available in the rich zone and which ultimately is partially converted to NO in the exhaust.

3.1.2 Primary Zone Stoichiometry (SR_1)

Figure 9 shows the influence of primary zone stoichiometry on exhaust NO emissions for a second stage stoichiometry of 0.9 and an overall stoichiometry of 1.25. These data indicate that exhaust emissions appear to increase only slightly as the primary zone stoichiometry is increased. However, it should be remembered that as the primary zone stoichiometry is increased, the amount of fuel added in the secondary zone must be increased proportionally to maintain a constant SR_2. Figure 10 shows these results replotted in terms of moles of NO in the exhaust relative to moles of NO exit in the primary and

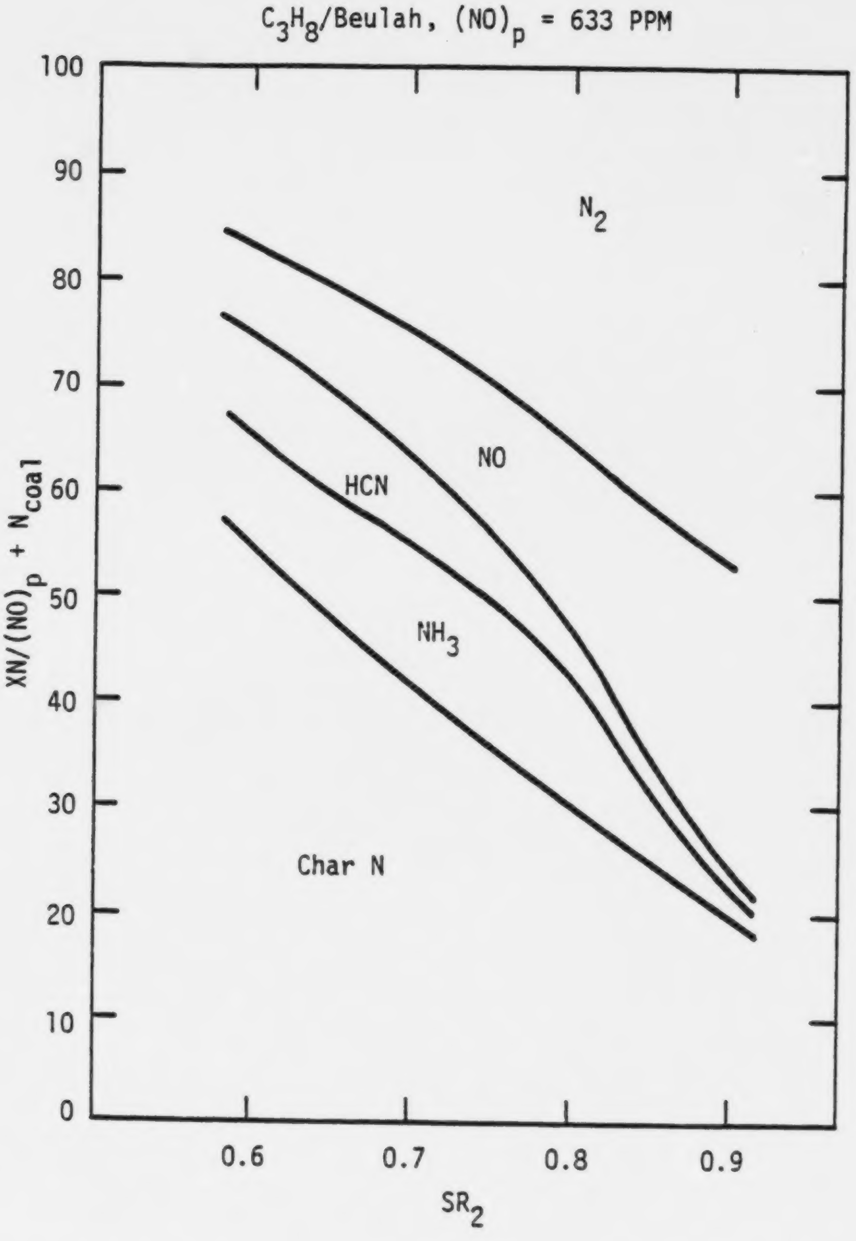

Figure 7. Fate of First-Stage NO and Coal Nitrogen, Second-Stage Exit.

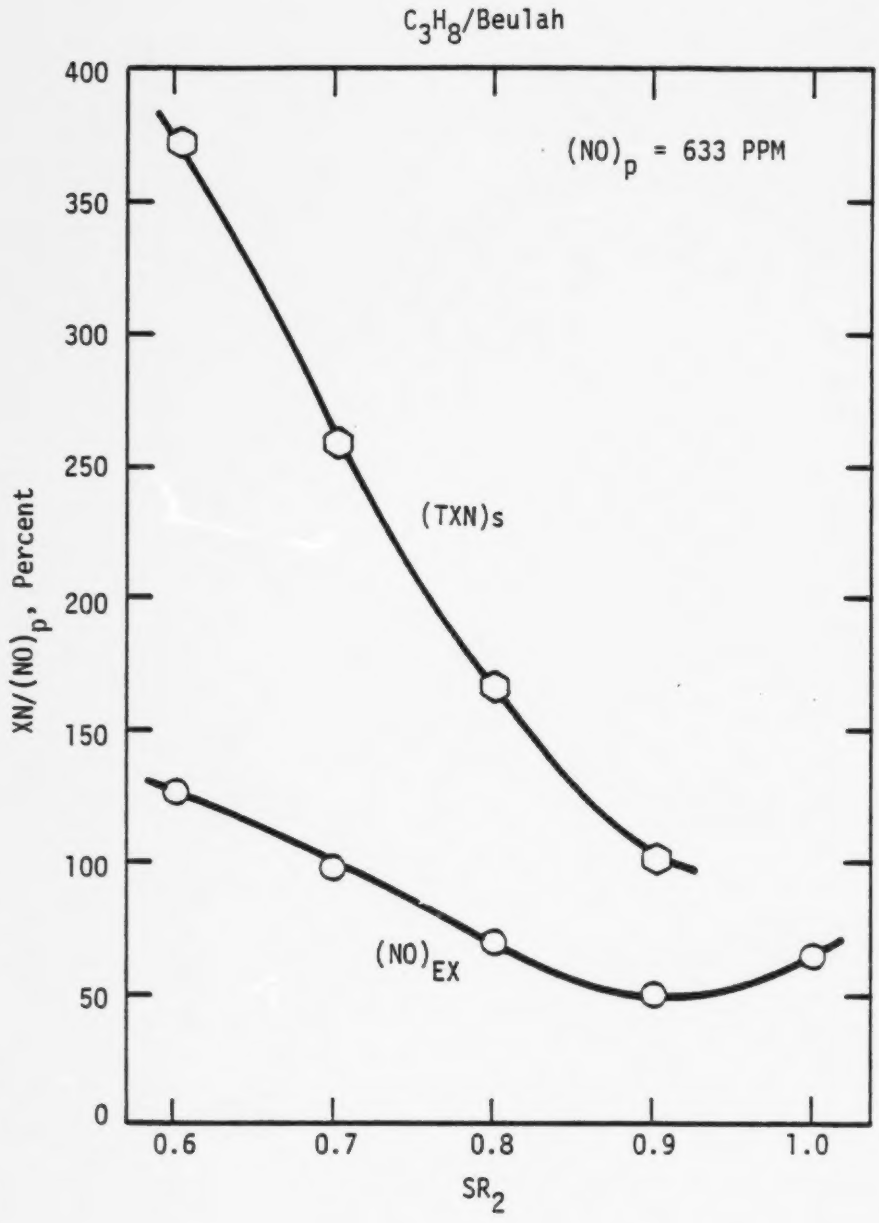

Figure 8. TXN Oxidation in the Third Stage.

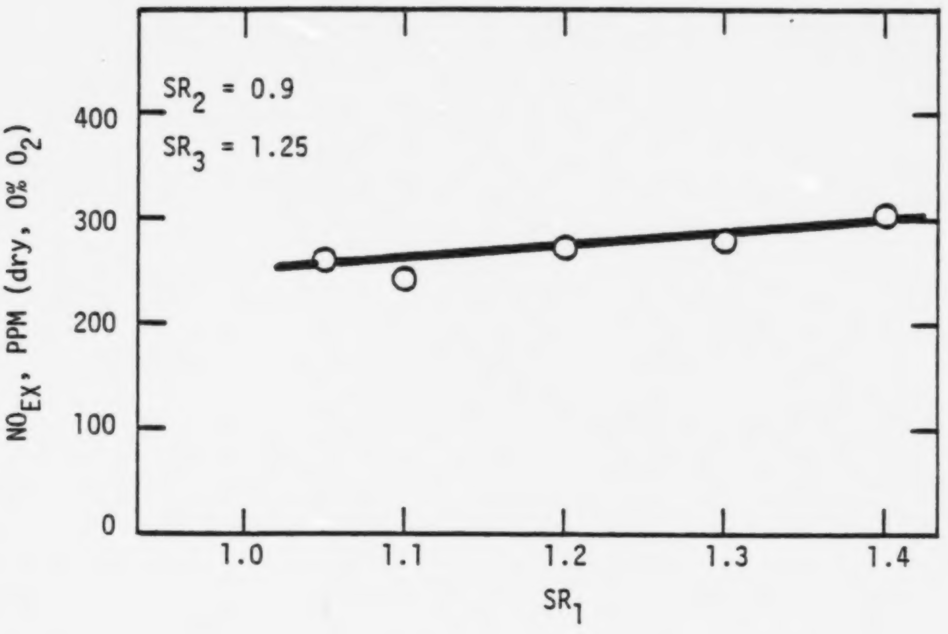

Figure 9. Influence of Primary Zone Stoichiometry on Exhaust NO Emissions.

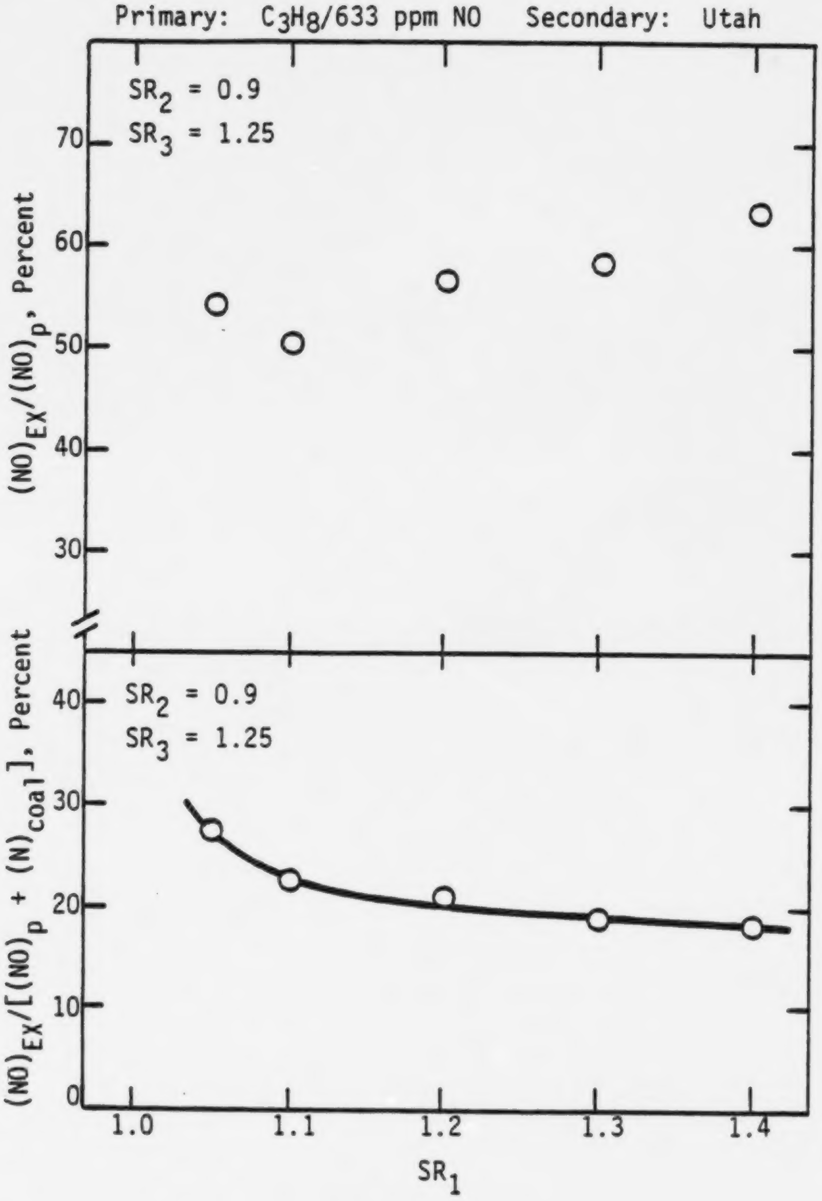

Figure 10. Influence of Primary Zone Stoichiometry on Apparent Conversion.

it illustrates that in fact, it is not desirable to operate at high primary zone stoichiometries. Increasing SR_1, increases the amount of fuel required to create a fuel-rich condition in the reburning stage and this in turn increases the available reactive nitrogen. Figure 10b shows that the conversion of the available nitrogen is essentially constant and, therefore, the emissions on either a volumetric (ppm) or a heat-release (lbs $NO_2/10^6$ Btu) basis remain essentially constant. However, in practice, it would not be desirable to operate at a high first-stage stoichiometry if it could be avoided because this would both increase the primary zone NO and increase the amount of heat-release required in the reburning zone.

3.1.3 Tertiary Zone Stoichiometry

Figure 11 shows the influence of the final (excess air) zone stoichiometry for a primary stoichiometry of 1.1 and a secondary stoichiometry of 0.9. As expected, the overall stoichiometry has little influence on the exhaust NO emissions. A 55 percent reduction in emissions was achieved in this reburing configuration for all overall stoichiometries studied.

3.2 Primary Zone NO Concentration

To establish the effect of the NO concentration at the inlet of the reburning zone, a series of experiments was conducted with varying primary NO levels. Figure 12 summarizes these results; all of the data are shown in terms of the exhaust NO to primary zone NO ratio. As noted previously, as the secondary zone stoichiometry is reduced, the exhaust emissions generally decrease, go through a minimum at approximately $SR_2 = 0.9$, and then increase due to the fuel nitrogen content of the reburning fuel. Figure 12 also indicates that the effectiveness of the reburning concept depends heavily on the initial NO level. If the initial NO level is high (e.g., 2887 ppm), reductions as large as 75 percent can be achieved with the reburning concept. However, if the NO level is relatively low (e.g., 148 ppm) reburning can increase the exhaust emissions at all conditions.

Figure 13 summarizes the effectiveness of the reburning concept at the optimum secondary zone stoichiometry ratio for the various primary NO concen-

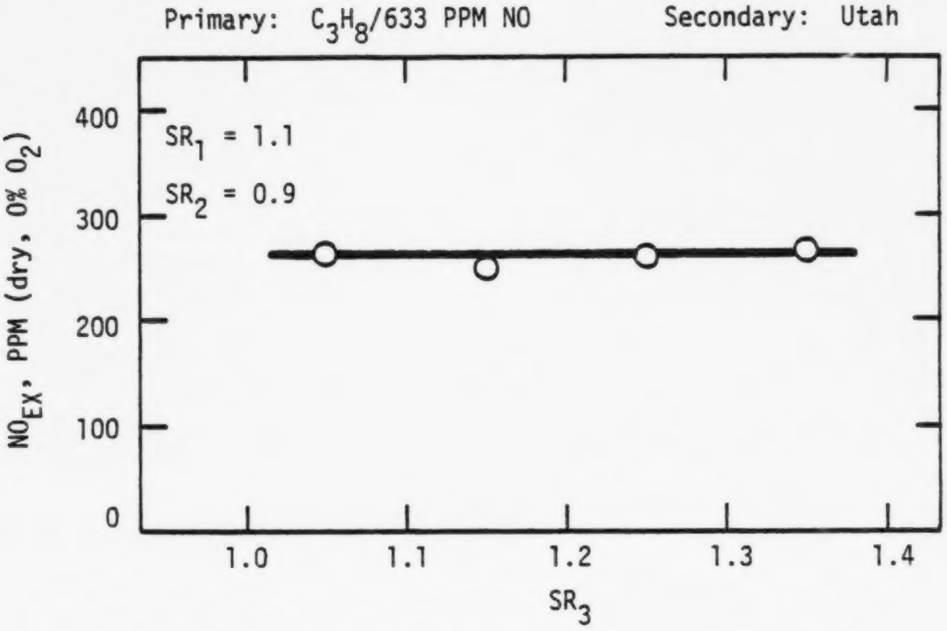

Figure 11. Effect of Tertiary (Overall) Stoichiometry on NO Emissions.

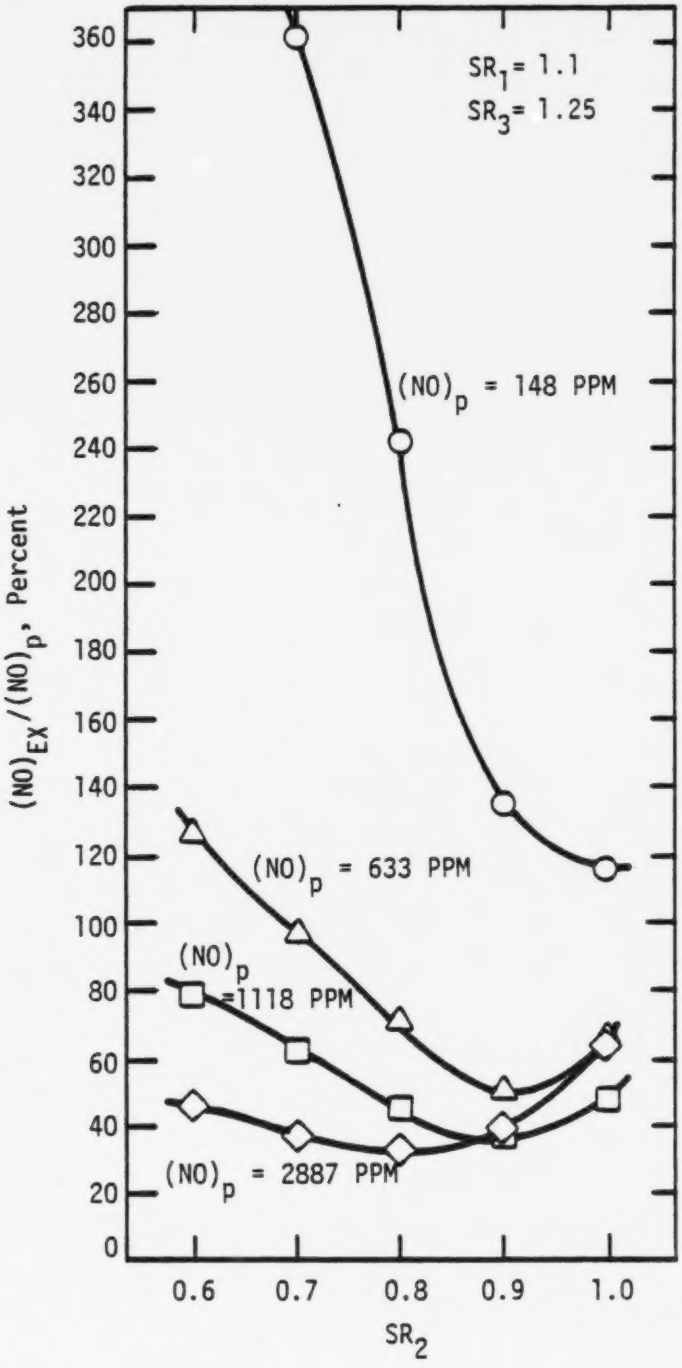

Figure 12. Influence of Primary Zone NO Concentration.

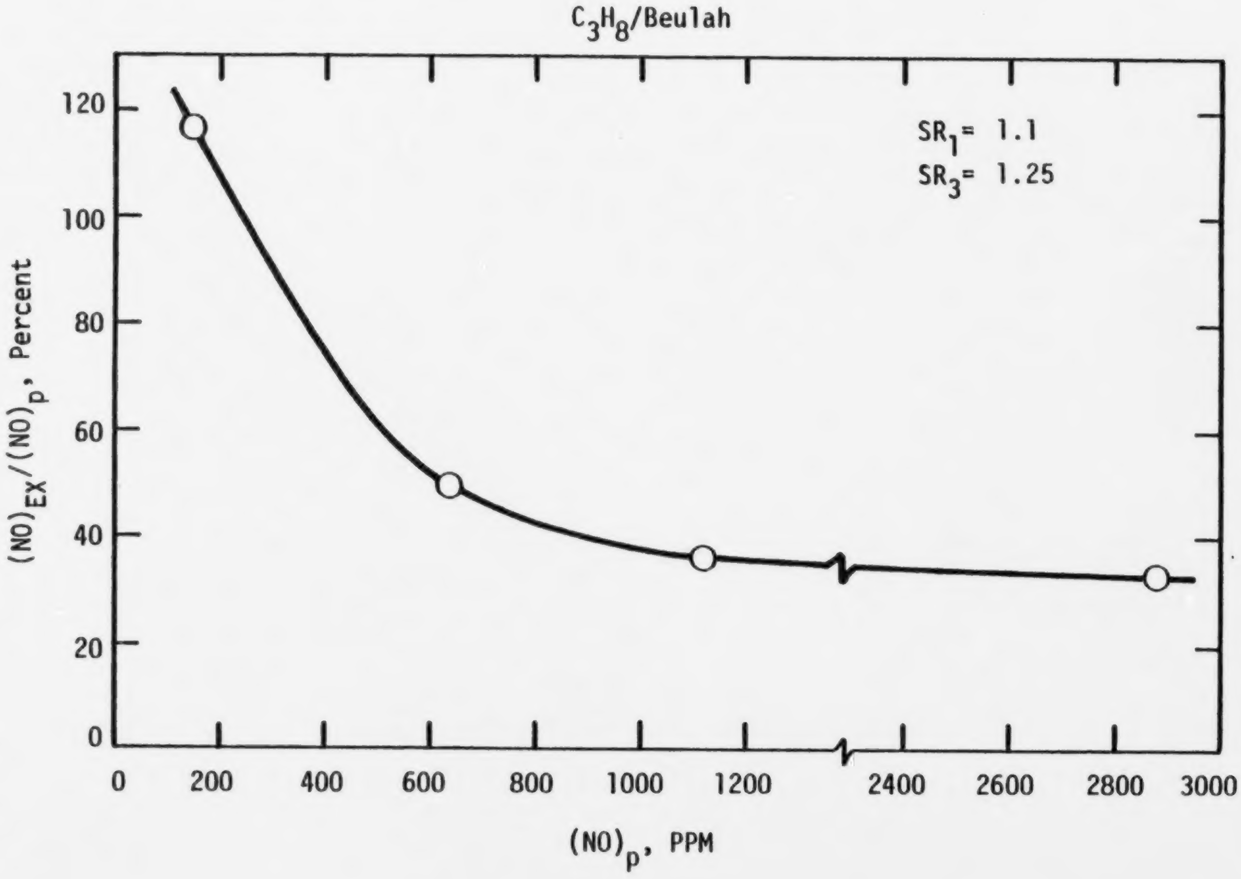

Figure 13. Effect of Primary Zone NO Concentration at Optimum SR_2.

trations. This figure emphasizes that it is unreasonable to assume the application of reburning will always result in a constant 50 percent reduction in the exhaust emissions. The effectiveness of the reburning process is clearly dependent upon the initial NO level (and upon the overall combustion conditions). Figure 14 summarizes all of the data taken with the propane/Beulah system for the different primary zone NO concentrations. In this case, the total NO in the exhaust (in moles per hour) is plotted against the molar flow rate of reactive nitrogen into the reburning zone (the primary NO + the nitrogen in the coal). The solid symbols are the four different initial NO concentrations without any reburning fuel present. As expected, the exhaust emissions increased essentially linearly with increasing primary NO when no reburning fuel was present. In general, as the reburning fuel is increased, the NO emissions decrease until they reach an effective "operating line". As further reburning fuel is added, the origin of the nitrogen becomes less important; increasing the reactive nitrogen content of the fuel-rich reburning stage, either by increasing the primary zone NO or adding additional fuel, results in increased NO emissions. Clearly the slope of the operating line is a strong function of the combustion conditions and the stoichiometry distribution throughout the furnace. However, its existence demonstrates the importance of the nitrogen content of the reburning fuel. If the primary zone NO concentration is low and below the overall operating line, then the addition of any reburning fuel will increase the exhaust NO emissions (circles).

3.3 Coal Composition

Figures 15 and 16 summarize the results of a series of experiments where the reburning fuel was changed from the Beulah-North Dakota lignite to the high-volatile Utah bituminous coal. In all cases, the primary fuel was propane. The North Dakota lignite contained 1.04 percent nitrogen (DAF) and the nitrogen appeared to be relatively non-volatile. (Only 21 percent was evolved as HCN in the solid pyrolysis experiment.) In contrast, the Utah coal contained 1.67 percent nitrogen (DAF) and a much larger fraction of the nitrogen was volatile (38.1 percent in the inert-pyrolysis tests). Tests were also attempted with the Rosa-Alabama coal because of its extreme tendency to

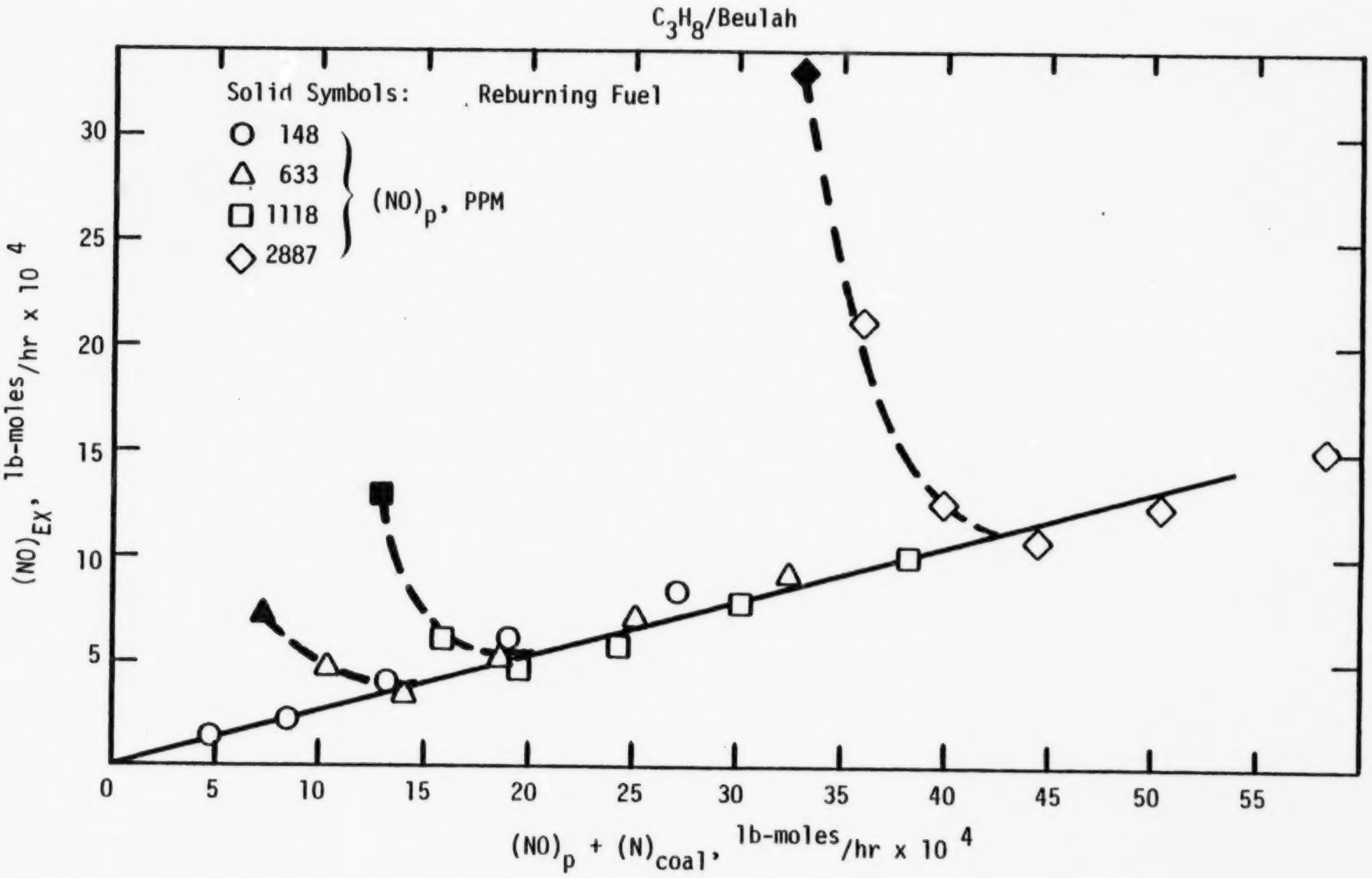

Figure 14. Importance of Total Available Nitrogen (Primary NO + Fuel Nitrogen).

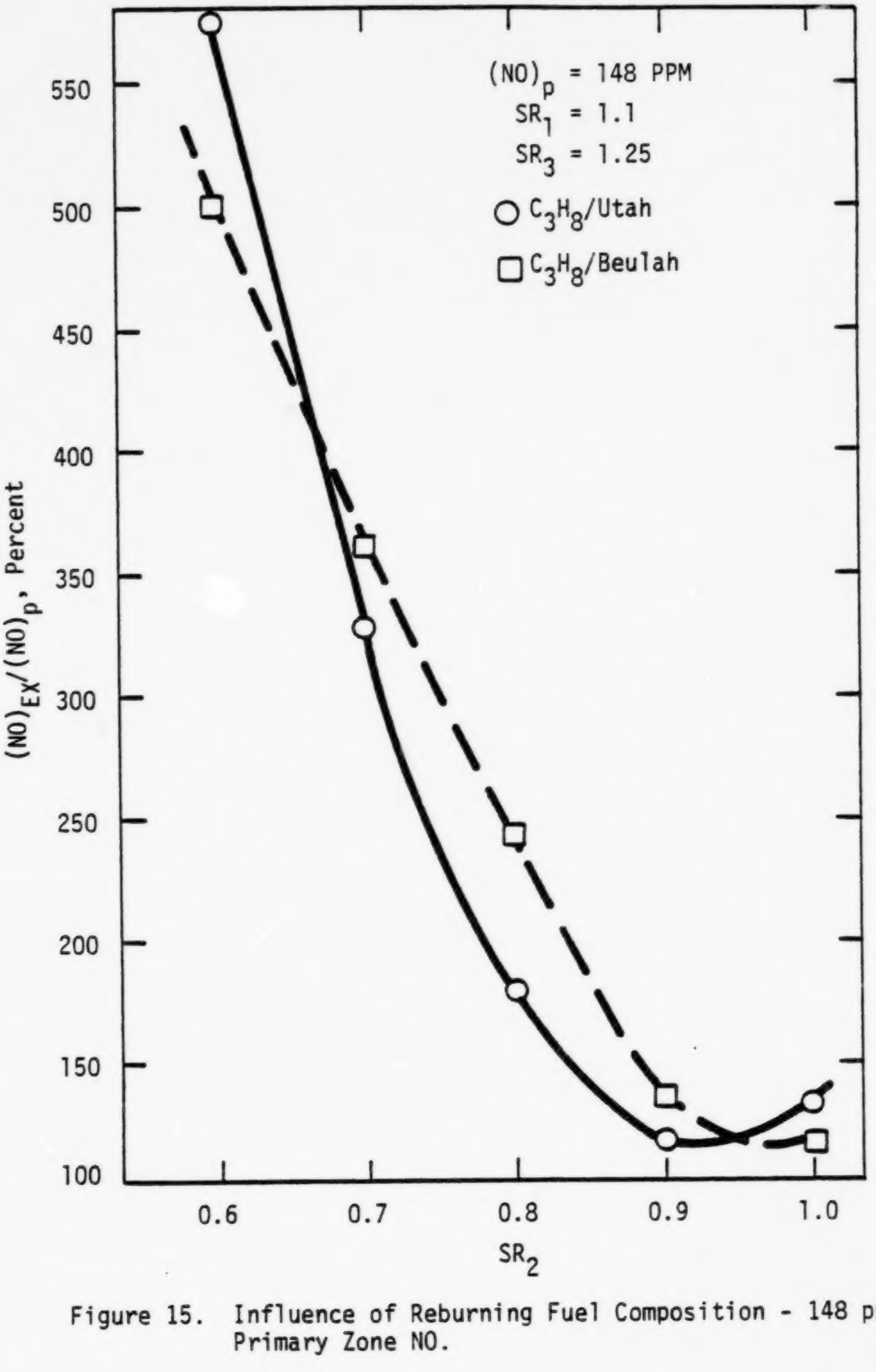

Figure 15. Influence of Reburning Fuel Composition - 148 ppm Primary Zone NO.

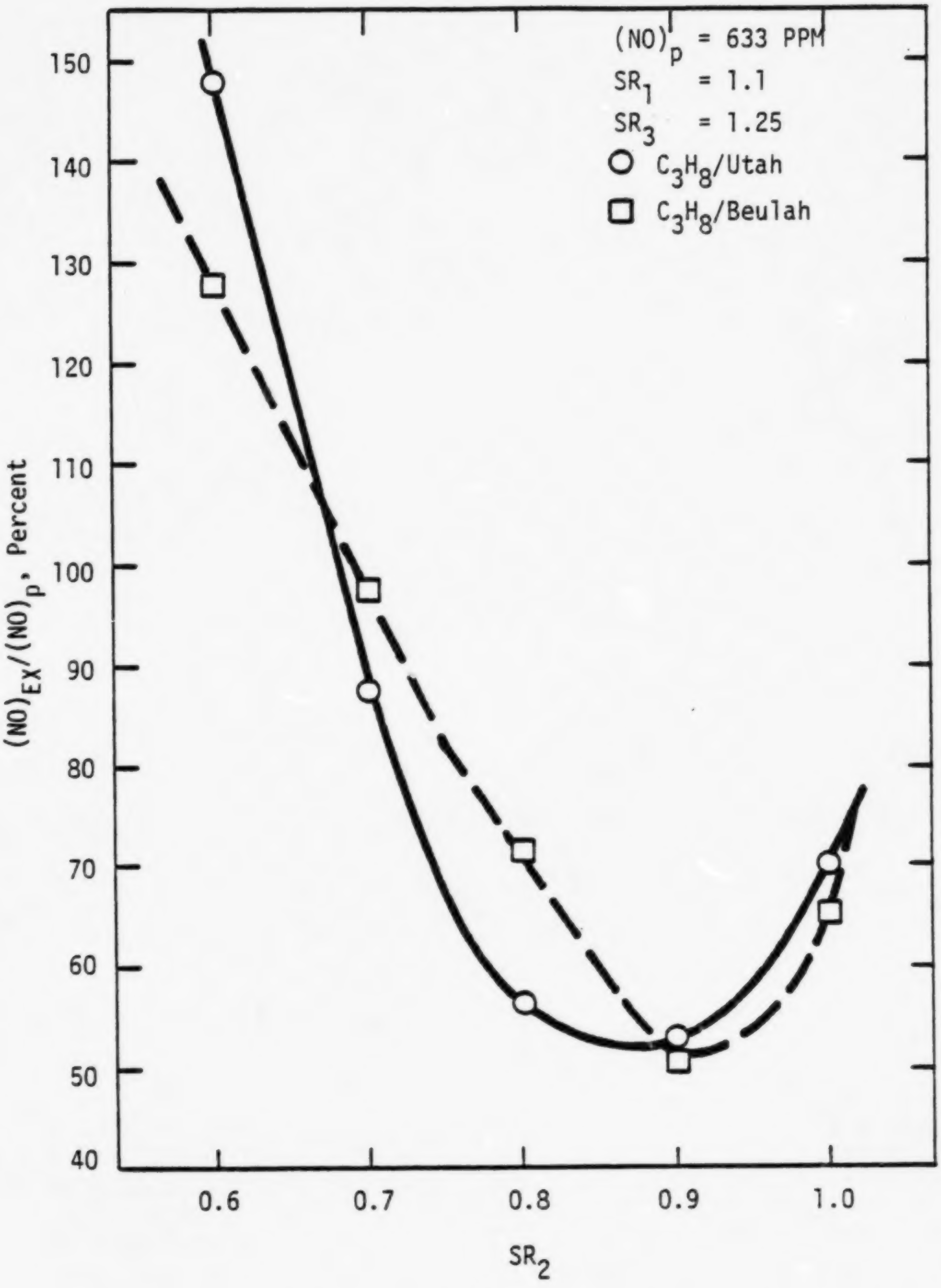

Figure 16. Influence of Reburning Fuel Composition - 633 ppm Primary Zone NO.

retain its nitrogen in the solid phase; however, it would not burn under any of the conditions tested.

The Utah and Beulah results shown in Figure 15 are for a primary zone NO concentration of 148 ppm and indicate that reburning increased the exhaust NO emissions under all conditions for both fuels. Figure 16 shows similar results for the 633 ppm NO primary and again approximately 50 percent reduction was achieved at the optimum secondary stoichiometry (0.9); however, at low stoichiometries emissions increased dramatically. Both fuels behaved approximately the same in terms of the effectiveness of the reburning concept. This trend was somewhat unexpected because the fuels differ significantly in both the total nitrogen content and in the distribution of that nitrogen. Figure 17 summarizes all of the data on a molar basis. The data indicate that the propane/Utah system behaves similar to the propane/Beulah, but for a given reactive nitrogen content in the reburning zone, the Utah coal (open symbols) produces less exhaust NO_x. This is believed to be because the nitrogen in the Utah coal is considerably more volatile and can be evolved easier in the fuel-rich reburning zone. The Beulah North Dakota lignite tends to carry more of its nitrogen into the final tertiary stage in the solid phase. This ultimately results in higher NO_x emissions for a given nitrogen level. Thus, these data suggest that the optimum reburning fuel is one which contains very little fuel nitrogen (e.g., the Japanese Taiheiyo coal) and that nitrogen should be highly volatile.

3.4 Thermal Environment

A series of studies was conducted to investigate the role of thermal environment on the effectiveness of the reburning concept. In these experiments, cooling coils were placed in the secondary (fuel-rich) stage. Figure 18 summarizes the overall results of these studies where propane was the primary zone fuel and the Beulah North Dakota lignite was the reburning fuel. Throughout the testing the primary zone stoichiometry was held constant at 1.1 and the overall stoichiometry was 1.25. Figure 18 illustrates that the addition of secondary cooling dramatically reduced the exhaust NO emissions for both primary zone NO concentrations (633 and 148 ppm). In an effort to

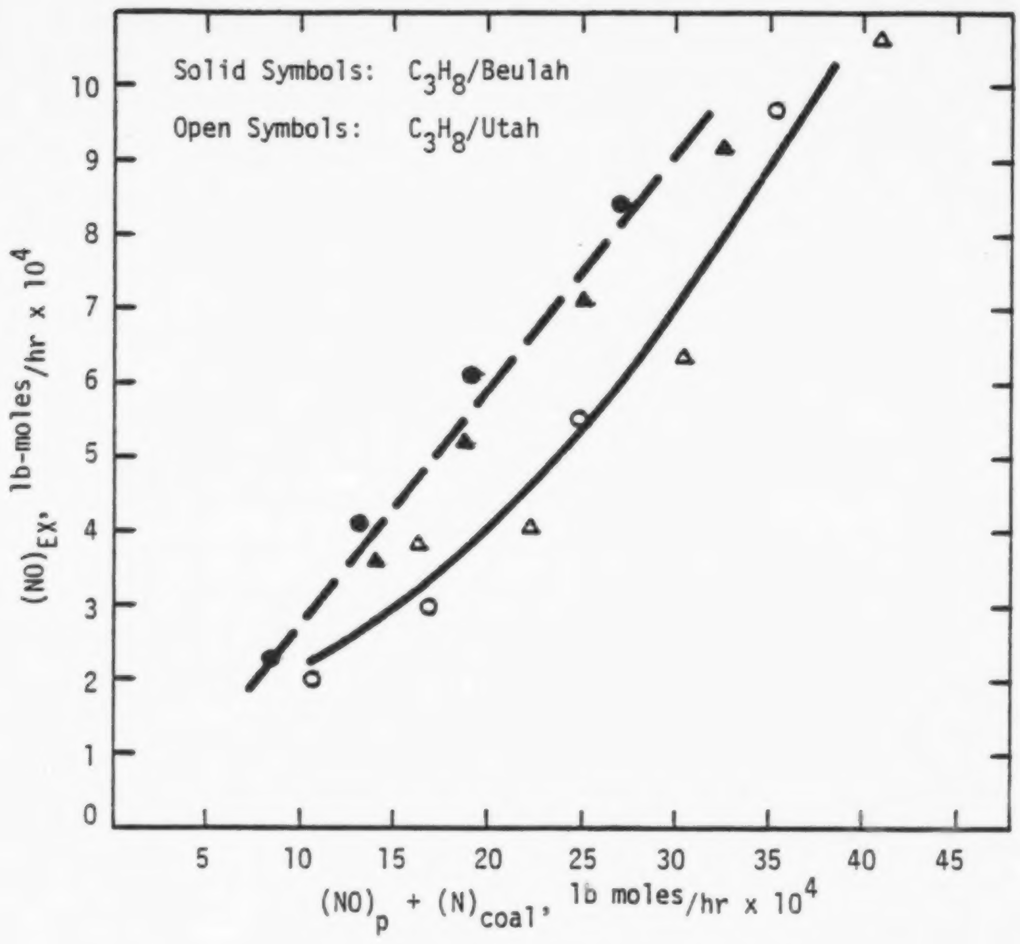

Figure 17. Importance of Fuel Nitrogen Volatility in Reburning.

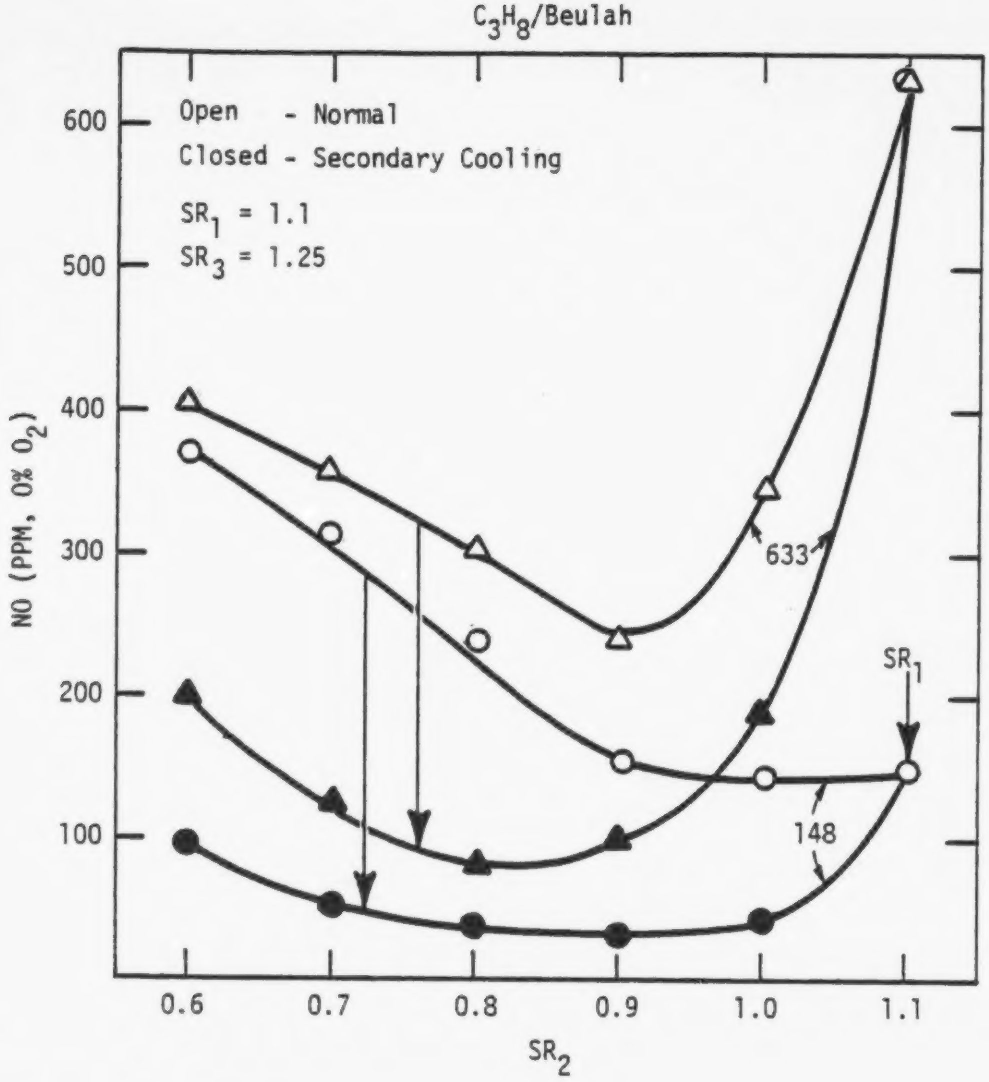

Figure 18. Effect of Secondary Cooling on Exhaust NO Emissions.

understand the mechanism of this effect, detailed XN species measurements were made at the outlet of the secondary (fuel-rich) zone and these results are summarized in Figure 19. Cooling had relatively little effect on the concentrations of HCN and NH_3 leaving the rich zone (except at the extremely low secondary stoichiometries); however, decreasing the temperature of the rich zone significantly decreased the rate of NO decay within the rich zone and resulted in a much larger char nitrogen carry-through. These results are essentially identical to those measured previously by Chen, et al(8). for normal staged combustion systems. Decreasing the temperature of the rich zone tends to retard both the formation of N_2 from the gas phase TFN species and the evolution of nitrogen from the solid phase. Figure 20a shows the overall TXN (including char nitrogen) for both the normal and cooled case. The significant increase in TXN with cooling is the direct result of the higher NO and char nitrogen concentrations. Figure 20b shows the overall conversion of the TXN to exhaust NO and indicates that the reason decreasing rich-zone temperature results in reduced exhaust emissions (Figure 18) is that the conversion of the reactive nitrogen which enters the tertiary stage, greatly decreases in the cooled case. (Admittedly, the overall conversion-phase shown in Figure 20b is an integrated average of the gas-phase and solid-phase conversion, but there can be little doubt of the overall effect of cooling.) The dramatic decrease in the TXN conversion at reduced temperatures is believed to be the result of selective NO reduction by NH_i species(8).

3.5 Summary

The propane/coal reburning studies have indicated that even for this simple system, the concept of reburning is not as simple as has been suggested by the Japanese(4). The effectiveness of the concept appears to depend heavily on the secondary zone stoichiometry, the coal composition, and the thermal environment. In principle, the reburning concept consists of two processes; NO reduction in a fuel-rich secondary-zone and TFN conversion in an oxygen-rich tertiary zone. The data shown in Figures 19 and 20 for the normal thermal environment indicate that with the propane/Beulah system at the optimum secondary stoichiometry (0.9) only approximately 60 percent of

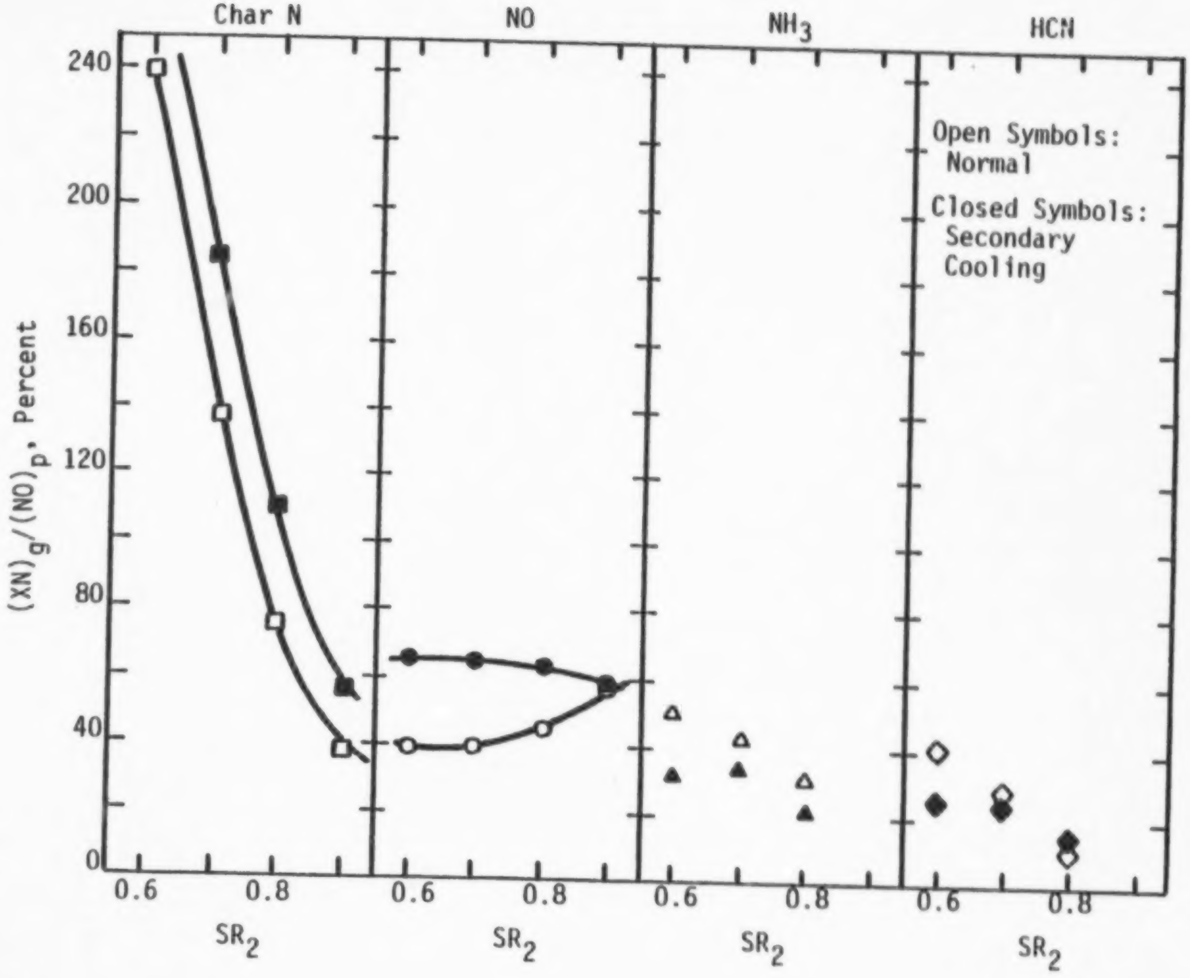

Figure 19. Effect of Secondary Cooling on Species Concentrations at the Second Stage Exit.

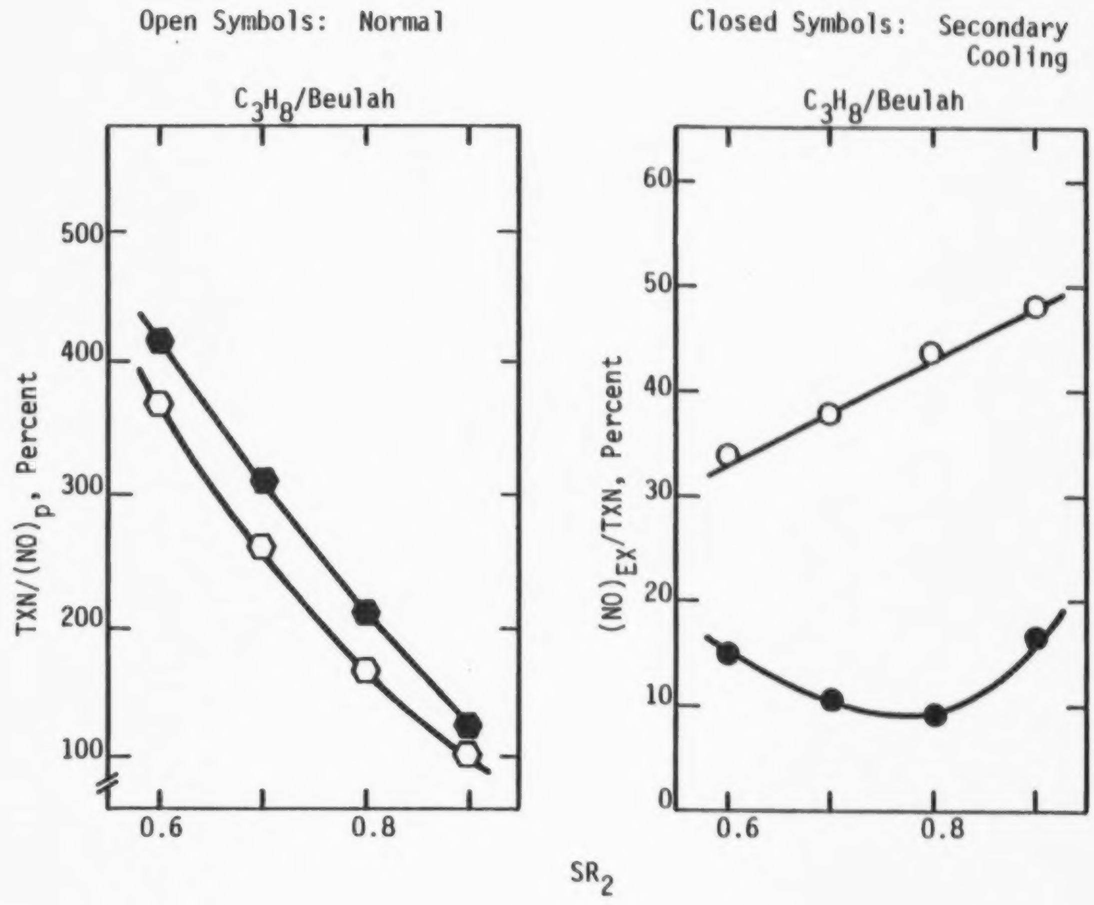

Figure 20. Secondary Cooling: Effect on TXN Formation and Conversion.

the primary zone NO survives the secondary, fuel-rich zone and this is in accordance with the Japanese work. However, char nitrogen equivalent to 40 percent of the primary NO may also be carried into the tertiary stage. The overall conversion of all of this nitrogen is approximately 50 percent. (Probably the average of a relatively high NO conversion, e.g., 80 to 90 percent and a relatively low char nitrogen conversion, e.g., 20 percent.) Thus, it is possible to achieve an overall emissions reduction of 50 percent under these conditions. Under the cool conditions at $SR_2 = 0.9$, the char nitrogen carry-through increases to the equivalent of approximately 60 percent of the initial NO. However, the overall conversion drops dramatically to below 20 percent resulting in an overall reburning effectiveness of about 75 percent.

In summary, these data suggest that the reburning concept will be most effective in systems which have the following characteristics:

- A high primary zone NO concentration.
- A highly volatile, low nitrogen reburning fuel.
- A secondary stoichiometry of approximately 0.9.
- A hot secondary zone to maximize TFN reduction and char nitrogen evolution.
- A cool tertiary zone to enhance the selective NO reduction by NH_i species.

4.0 COAL/COAL RESULTS

This section of the report describes the experimental studies which were conducted with a pulverized coal in both the primary and reburning stages of the reactor. Both the Utah and Beulah coals were used in this portion of the work, but in all tests, the same coal was used in both stages.

4.1 Composition Effects

Figure 21 compares the results obtained with the Utah/Utah coal to those discussed previously from the propane/Utah coal studies. In both cases the primary zone NO was approximately 1100 ppm. The coal/coal results exhibit a secondary zone stoichiometry dependence essentially identical to that measured in the propane/coal studies, but the reburning concept was found to be more effective when the first-stage fuel was propane. Figure 22 shows a similar comparison for the Beulah-North Dakota lignite. In this case, the primary zone fuel had little influence on the effectiveness of the reburning concept at the optimum secondary zone stoichiometry.

Figure 23 compares the results obtained with the Utah coal to those obtained with the Beulah lignite. In this figure, the data are plotted on an emission factor basis. The Utah coal contains approximately 60 percent more fuel nitrogen than the Beulah coal and the uncontrolled NO emissions from the Utah coal are approximately 60 percent higher (1028 ppm vs. 625 ppm). However, under the optimum reburning conditions ($SR_2 = 0.8$) the emissions from the Utah coal were only about 30 percent higher than those from the Beulah system. This is believed to be because the nitrogen in the Utah coal is more volatile and therefore more desirable in a reburning system. The nitrogen in the Beulah lignite tends to remain in the char and is therefore more likely to be carried into the tertiary zone in the solid phase. Figure 23 illustrates that the effectiveness of the reburning concept depends strongly on both the initial uncontrolled emissions and on the fuel chemistry.

4.2 Thermal Environment

Figure 24 shows the effect of secondary cooling on reburning with the Beulah coal. Data are shown for both the propane primary and the Beulah

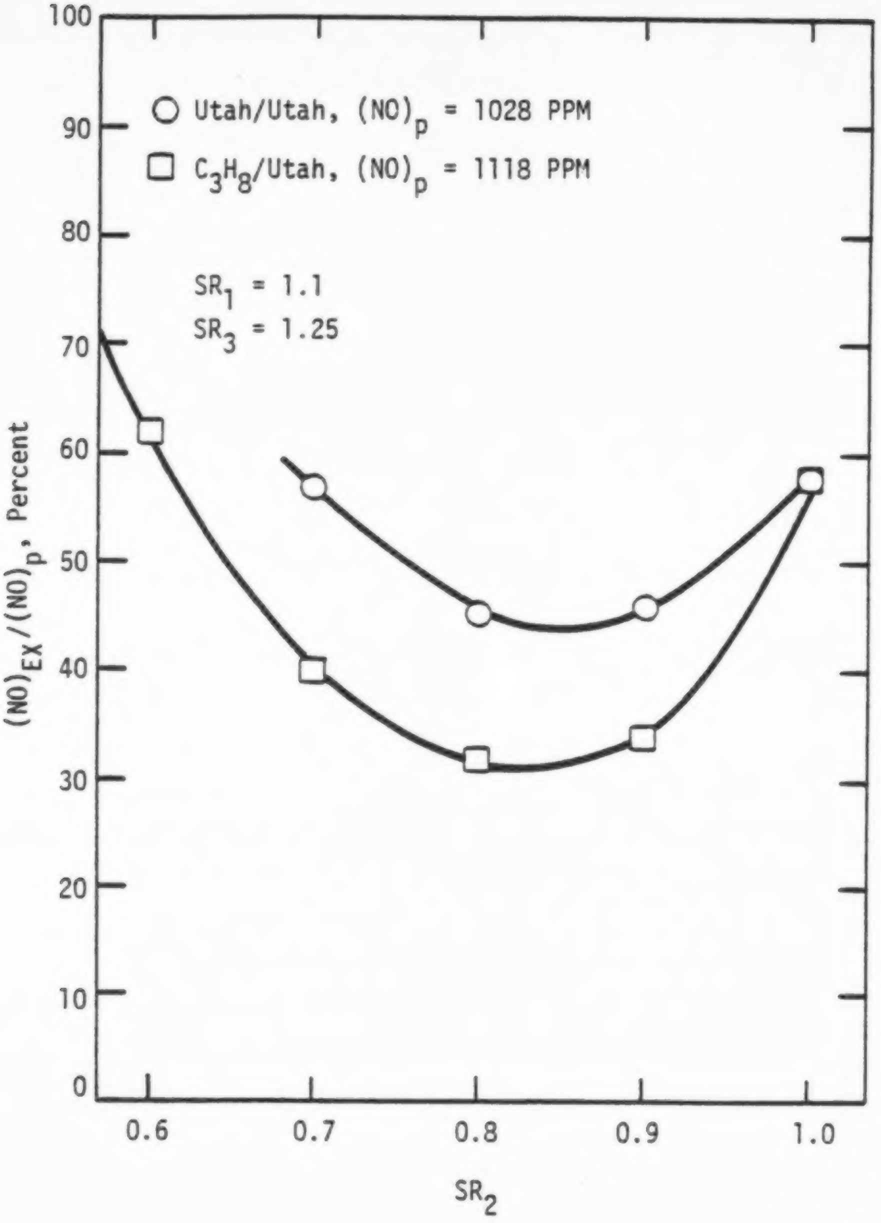

Figure 21. Influence of Primary Zone Fuel - Utah.

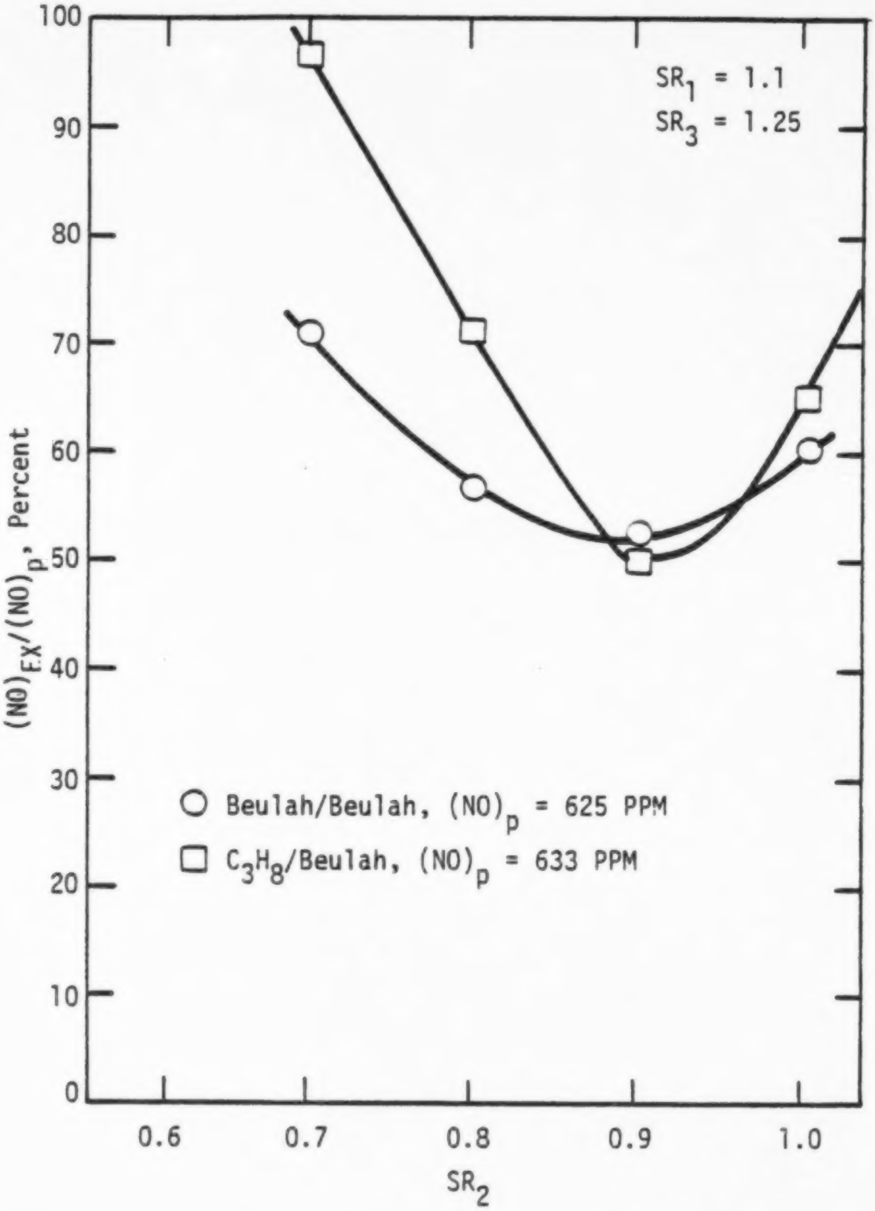

Figure 22. Influence of Primary Zone Fuel - Beulah.

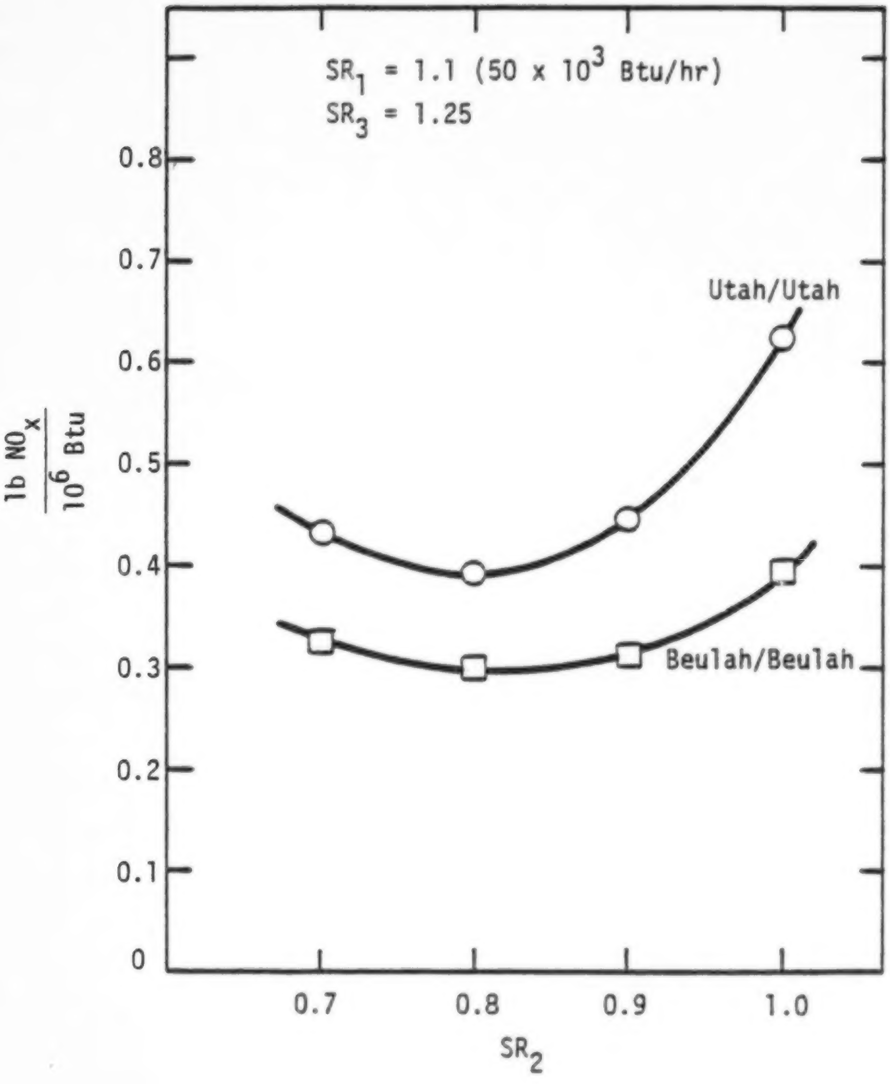

Figure 23. Overall Effect of Fuel Composition.

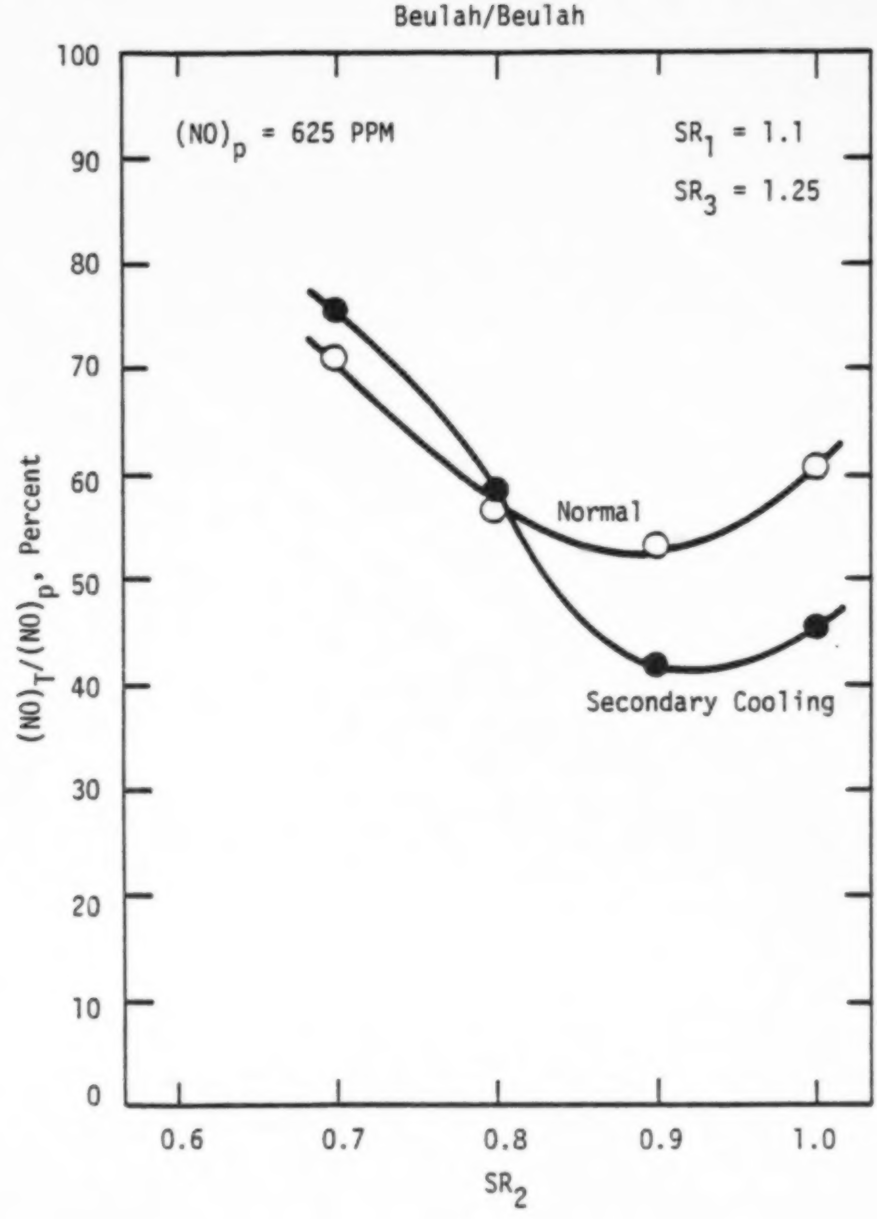

Figure 24. Effect of Primary Zone Fuel on Secondary Cooling Influence.

primary. These data indicate that cooling was far more effective with the propane primary than with the coal primary. In an attempt to understand this phenomena, detailed temperature measurements were made at the exit of all three combustion zones and these data were shown in Figure 25. As expected the coal primary produced higher first-stage exit temperatures (T_1). However, the secondary cooling coil had far less effect on the second-stage exit temperatures when both stages were fired with coal. This may be due to large differences in the flame radiation caused by the great increase in particle loading. Therefore, it appears that the reason secondary cooling did not greatly enhance the effectiveness of the reburning in the coal/coal case was because the gas temperatures were not sufficiently reduced.

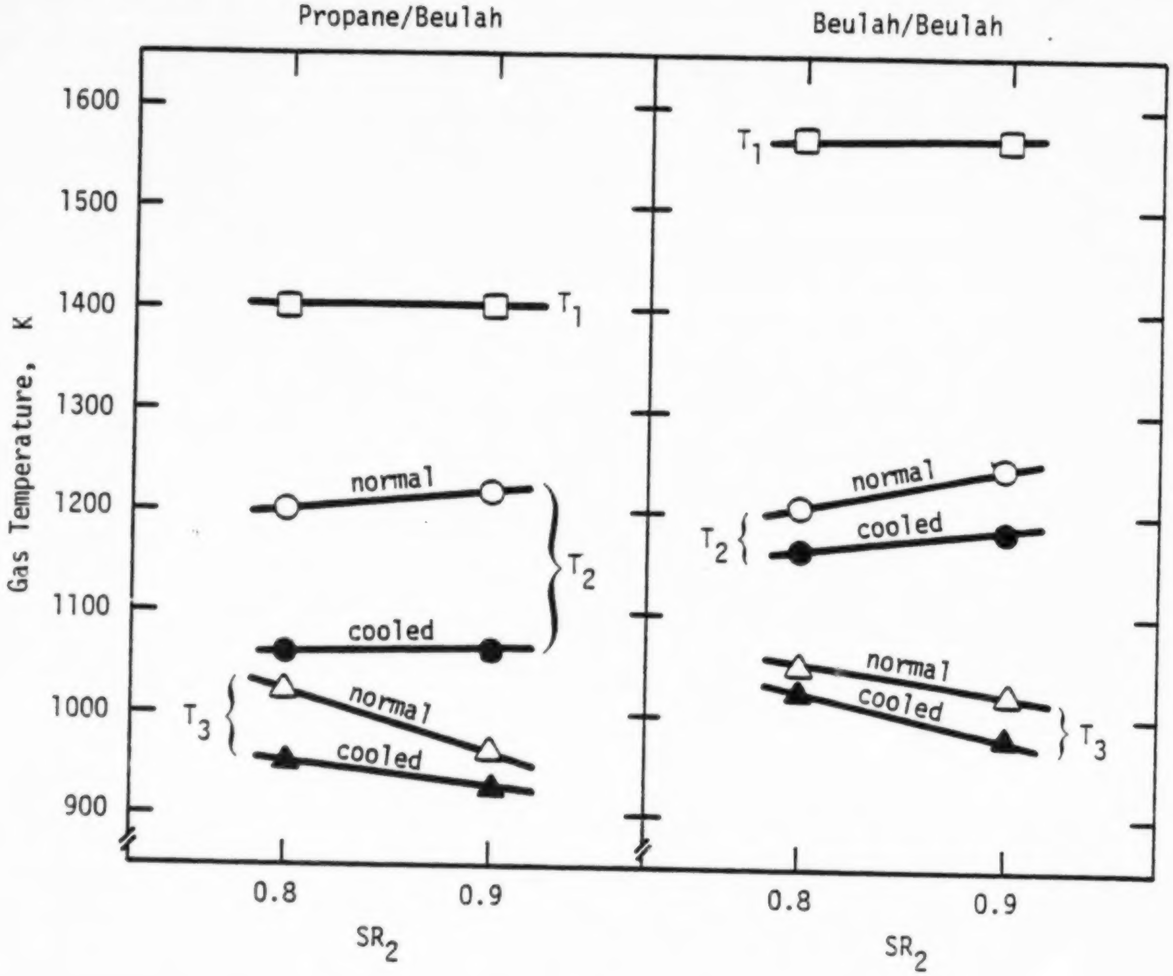

Figure 25. Detailed Temperature Measurements.

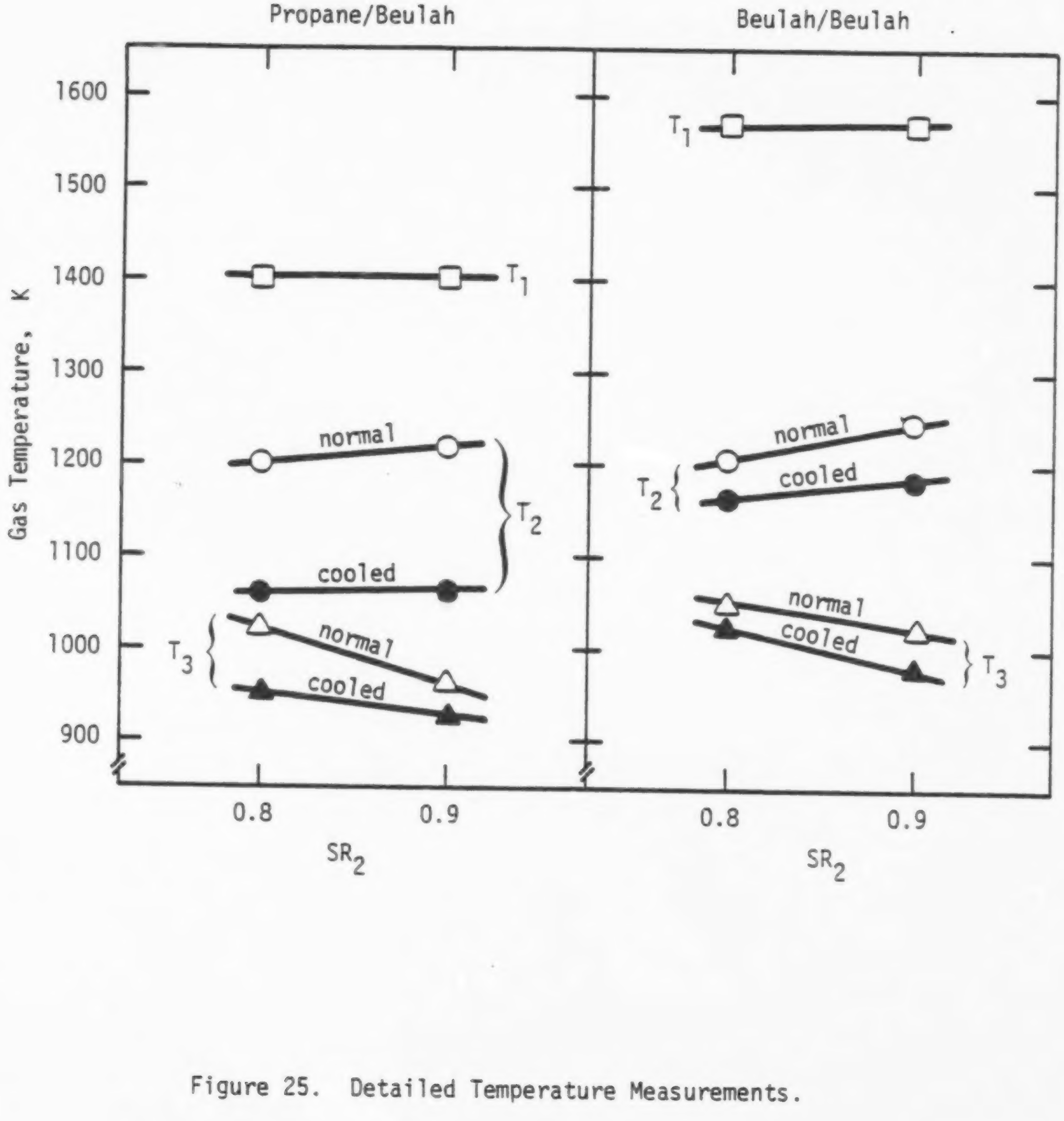

Figure 25. Detailed Temperature Measurements.

5.0 MIXED COAL RESULTS

To further investigate the effect of reburning fuel composition, a series of tests was conducted in which the primary zone fuel was the Utah coal and the reburning fuel was the Beulah lignite. Figure 26 shows these results under both normal and secondary cooling conditions for a primary zone stoichiometry of 1.1 and a tertiary stoichiometry of 1.25. As in the case of the propane/coal data, large reductions were achieved with the addition of secondary cooling. (It was not possible to obtain comparable data with the Utah/Utah system because it could not be fully burned out under the cooled conditions.) Figure 26 indicates that at the optimum secondary stoichiometry, the reburning effectiveness was approximately 80 percent.

Figure 27 summarizes all of the mixed coal results, and again emphasizes the importance of the primary variables: coal composition, secondary zone stoichiometry, and thermal environment. Comparison of the Utah/Utah and Utah/Beulah data indicates that the Utah coal is an inherently better reburning fuel (lower operating line) because its nitrogen tends to be more volatile; however, the Utah coal is hindered by its high total nitrogen content. Further, the Beulah coal has the advantage that it burns out more easily and therefore can be utilized in the extremely effective cooled secondary configuration. In addition, the Beulah coal produces large amounts of NH_3 under staged combustion conditions and this enhances the selective destructive of NO when the secondary cooling is present.

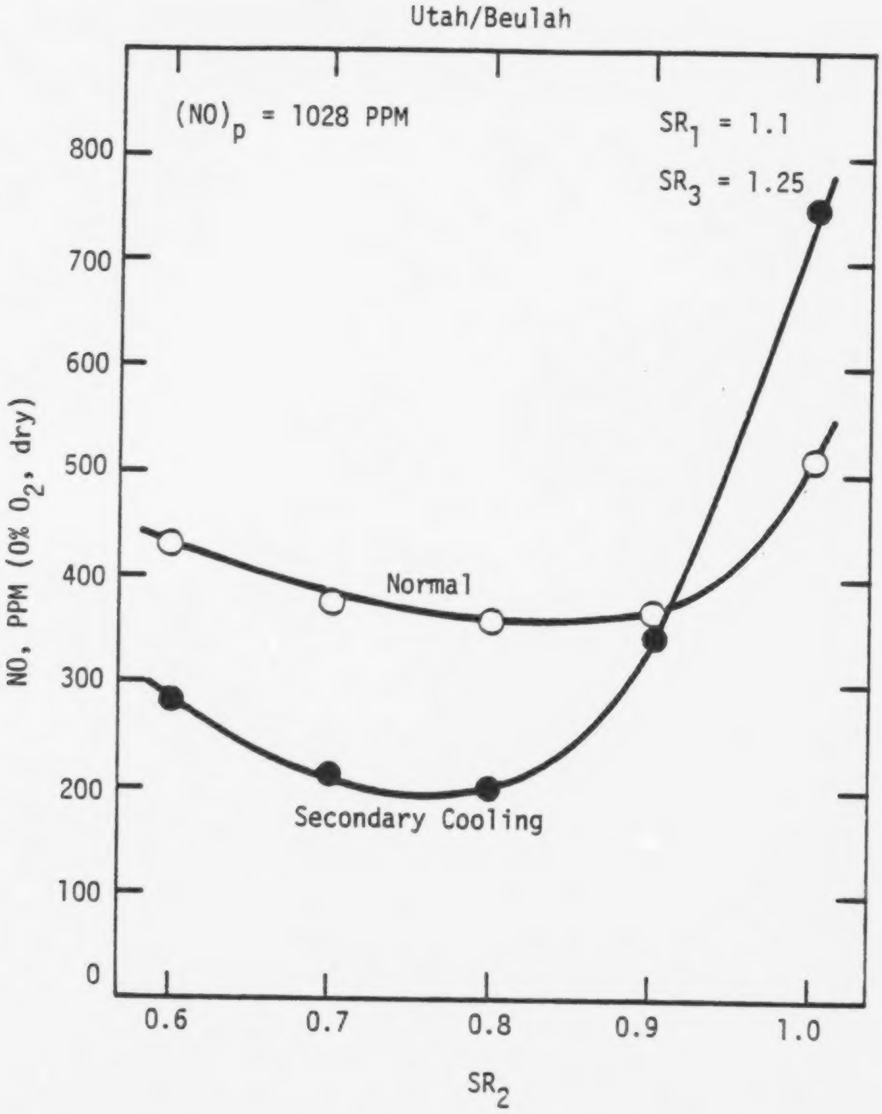

Figure 26. Mixed Coal Results.

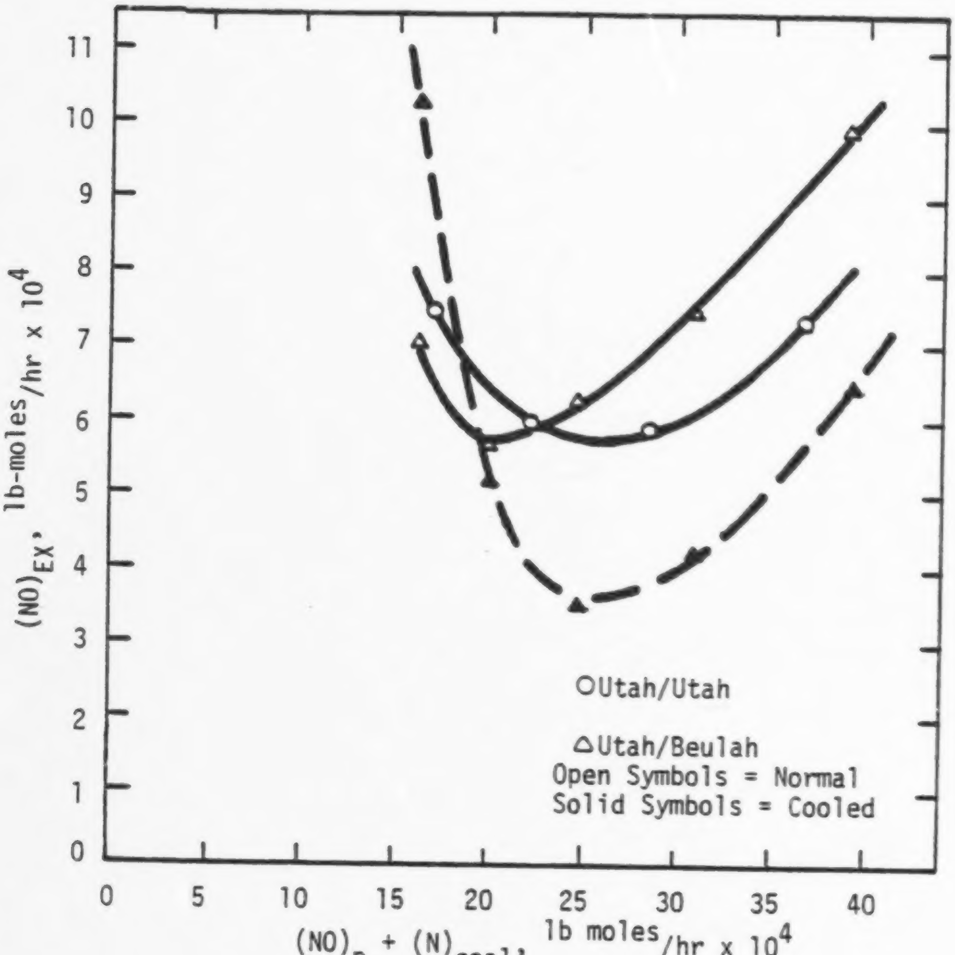

Figure 27. Importance of Reburning Fuel Composition and Secondary Cooling.

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